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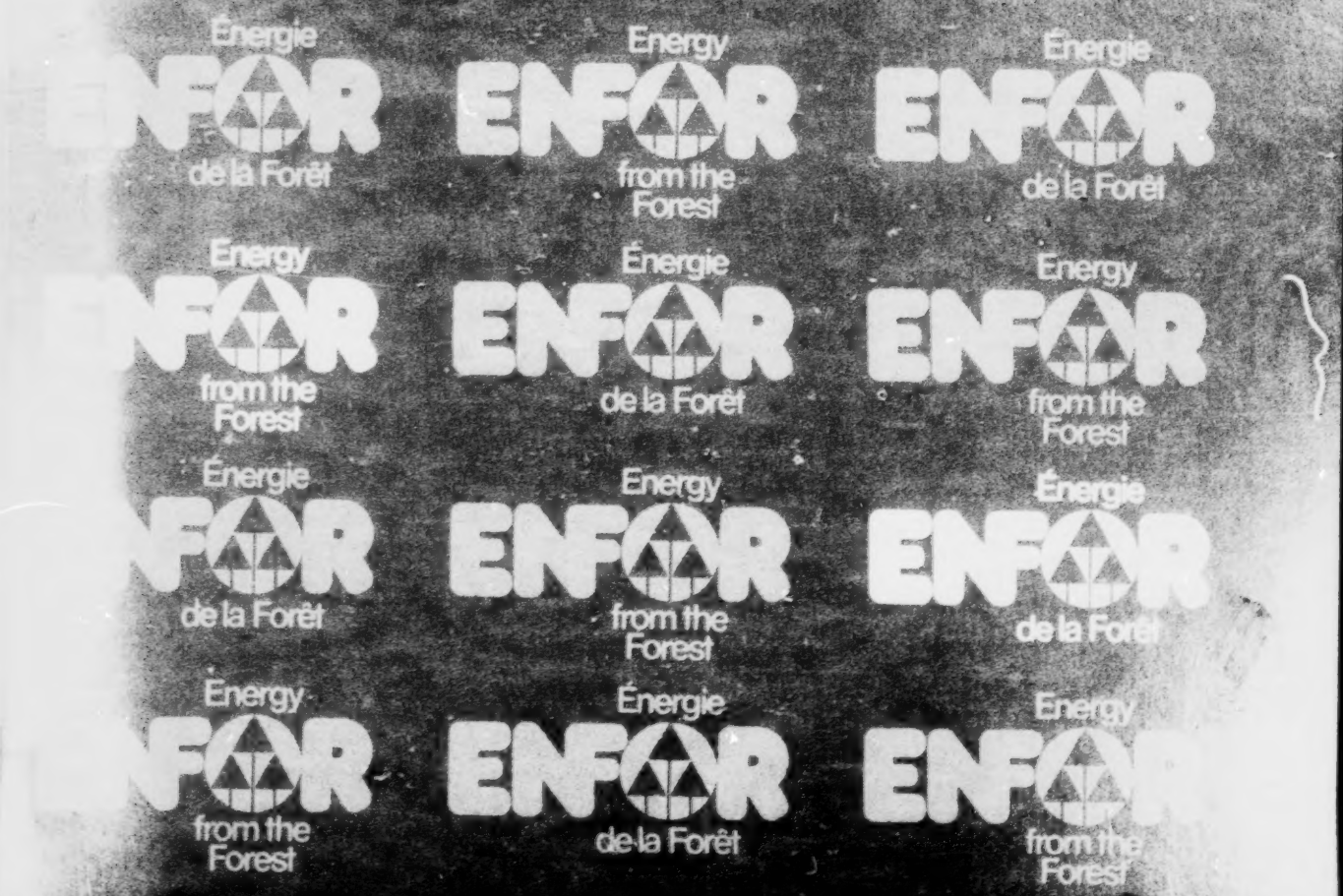
Chemicals from Forest Products by Supercritical Gas Extraction

Phase III

by

Elizabeth C. McDonald, John Howard &
Bridie Bennett



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ENFOR Project C-51

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Phase III

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CHEMICALS FROM FOREST PRODUCTS BY SUPERCRITICAL GAS EXTRACTION

ENFOR PROJECT C-51

ABSTRACT

Supercritical gas extractions of green sawdusts resulted in liquid products. Yields of extract were in excess of 70% when acetone or methanol at 350°C and 28 MPa were used. Similar yields could be obtained at lower extraction temperatures (260°C) and pressures (10 MPa) when the wood was pretreated with acid.

Extracts obtained using acetone (350°C and 260°C) and methanol (350°C) at 10 MPa were examined for chemical composition and also evaluated as substitutes for phenol in phenol-formaldehyde adhesives. Analyses for elements, calorific value and methoxyl content were performed. Levoglucosan and substituted guaiacols were identified in the complex products. Up to 30% of the phenol in phenolic resins could be substituted by acetone extract for waferboard adhesives.

The chemical composition of supercritical gas extraction products indicates that they would not be directly marketable as liquid fuels. Further processing of the products would be required to obtain marketable commodities.

An economic analysis based on laboratory experiments indicated that product cost would be $42 a barrel for an 800 barrel per day plant, excluding land and wood costs.

Resin and fatty acids were recovered from chipped Southern Pine using supercritical carbon dioxide, nitrous oxide, propane or ethylene. Yields were higher when propane or nitrous oxide was used, compared to those obtained using carbon dioxide or ethylene. For instance, a yield of 19% was obtained at 21 MPa by extraction with propane and 7% with nitrous oxide, but only 2% when carbon dioxide or ethylene was used. Higher pressures resulted in higher yields. Similar yield differences were observed between propane and nitrous oxide and the other gases when waxes were extracted from the bark of Douglas-fir.

The yields of chemicals by supercritical gas extraction were equal to or greater than those by solvent extraction. Supercritical gas extraction gave products which would be marketable directly. The application of this technique could reduce the use of petroleum-based solvents for the isolation of chemicals from forest products.

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1.0 INTRODUCTION

1.1 Objective

The ENFOR Biomass Conversion Sub-program is concerned with process technology for the conversion of forest biomass into energy, prepared fuels or industrial chemicals that will significantly reduce traditional fossil fuel consumption patterns.

The objectives of this work were to investigate the production of liquid fuels and the isolation of chemicals from forest products using gases above their critical temperature and pressure.

1.2 Background

Gases compressed beyond their critical pressure (Pc) and heated above their critical temperature (Tc) become supercritical fluids which can extract relatively nonvolatile compounds from forest products.

High temperature extractions (260°C-400°C) employing supercritical fluids which are normally liquid at room temperature have been the subject of intensive study for the isolation of liquid fuels from coal (Whitehead, 1981. Williams, 1981; Maddocks, 1979). However, supercritical gas extraction of wood has received less attention. Supercritical gas extractions of spruce wood have been carried out using acetone, tetrahydrofuran, dioxane and toluene with analysis of extracts for phenolic compounds (Calimli, 1978). The liquefaction of birchwood has been investigated using alcohols and alcohol - water mixtures with evaluation of the processes as an alternative chemical pulping technique (Köll, 1979).

Low temperature extractions (15°C-100°C) employing supercritical fluids which are normally gaseous at room temperature can selectively extract chemicals from natural products. Supercritical gas extraction is particularly effective for the isolation of substances of medium molecular weight and relatively low polarity. Its principal advantage over distillation is that separation can be accomplished at moderate temperatures, and in consequence can be applied to the recovery of heat-labile substances of low volatility.

Use of supercritical carbon dioxide (Pc, 7.4 MPa; Tc, 31°C) as an extractant for materials has grown rapidly in recent years. Among these uses are the decaffeination of coffee, removal of nicotine from tobacco and the extraction of flavours and fragrances. A recent patent covered the extraction of pinewood with carbon dioxide to produce tall oil, turpentine and rosin acids (Fremont, 1981). Propane (Pc, 4.3 MPa; Tc, 96.8°C) is used in the petroleum industry for deasphalting of heavy petroleum fractions (Williams, 1981).

2.0 EQUIPMENT AND METHODS: HIGH TEMPERATURE EXTRACTIONS

2.1 Equipment

The equipment shown in Figures 1 and 2 was used to extract liquid products from wood. A 34 MPa liquid metering pump (Milton Roy) was connected by a preheating coil to the base of a Kuentzel extraction vessel (Autoclave Engineers). The pressure was controlled by a valve (Snotrik) at the top of the extraction vessel. The sample and gas were heated in a fluidized sand bath (Techne). The low pressure outlet of the valve was connected to a flask and condenser, the flask serving as a catchpot for the extract and solvent. A gas meter (Canadian Meter) was used to measure the volume of noncondensible gases.

2.2 Operating Procedure

The extraction vessel was filled with 30 grams of lightly compacted wet wood (<4 mesh). The vessel was checked for leaks by pumping the solvent into the vessel with the valve closed until the pressure exceeded the experimental pressure by about 4 MPa. The pressure was then released and the extract collected in a flask. The vessel was lowered into the bath with the pump off and the valve open slightly. The valve was connected to the catchpot, the pump started and the operating pressure maintained by manually adjusting the valve. After the required extraction time the pump was stopped, the pressure released and the vessel removed from the bath. After cooling, the valve was removed and rinsed with an acetone and water mixture (4:1). The valve rinsings and the extract from the leak test were added to the extract collected in the catchpot.

Figure 1

SUPERCRITICAL GAS EXTRACTION APPARATUS EMPLOYING FLUIDS WHICH ARE LIQUIDS AT AMBIENT TEMPERATURE

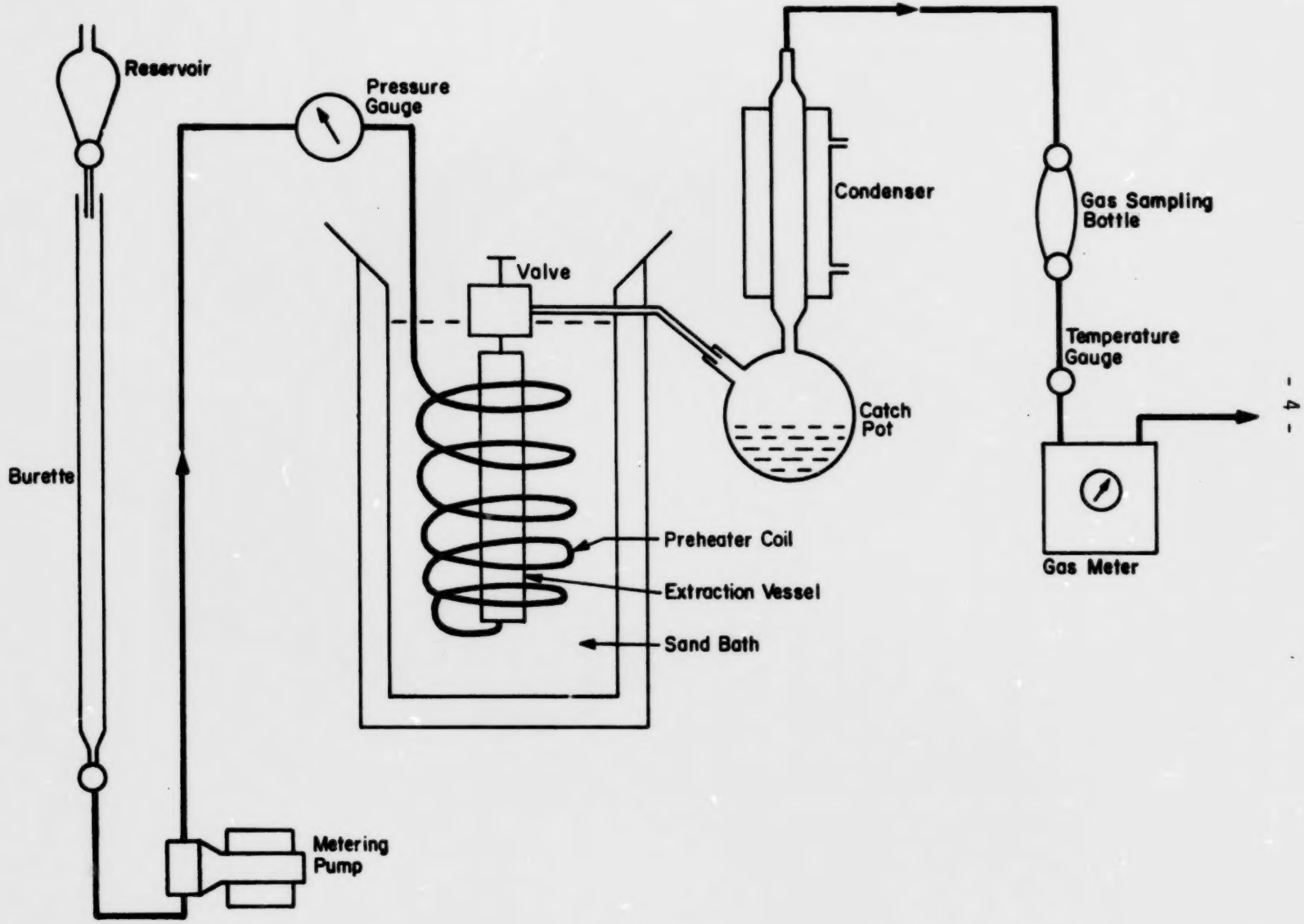
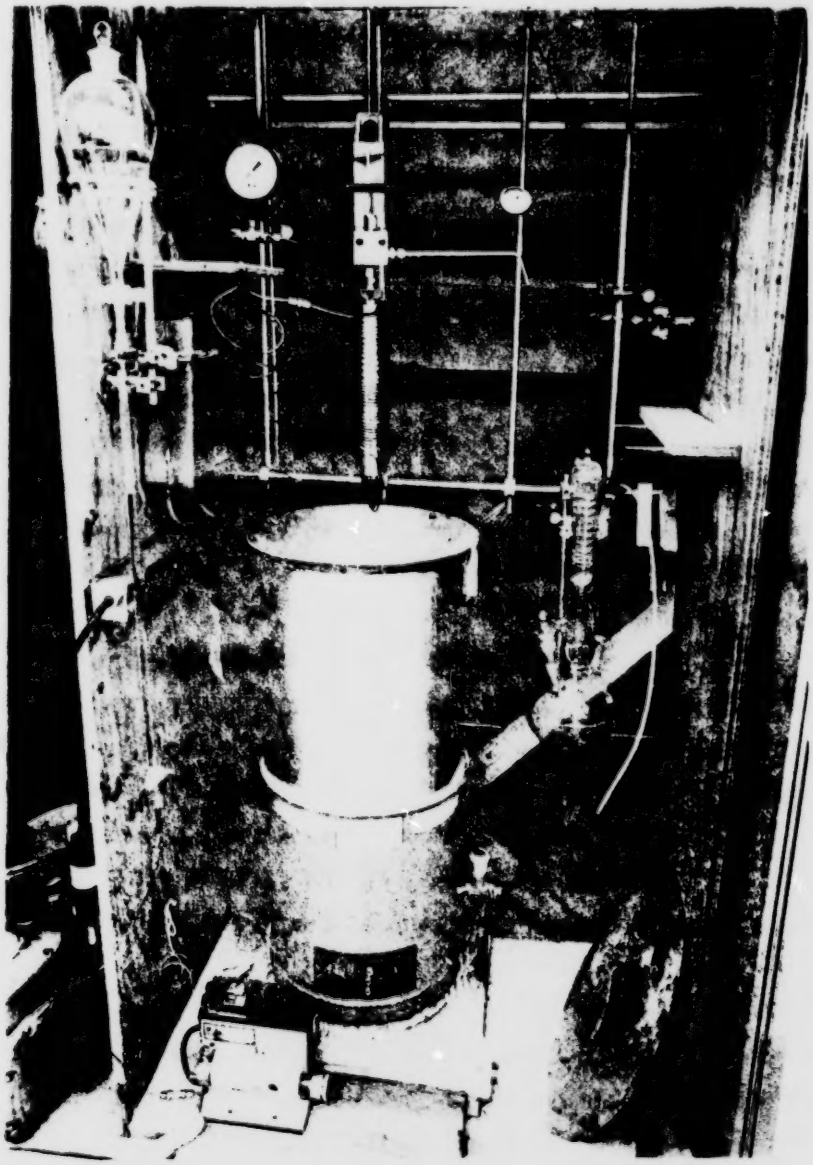


Figure 2 (24092.4A)

HIGH TEMPERATURE SUPERCRITICAL GAS EXTRACTION OF WOOD: OVERALL VIEW OF EQUIPMENT WITH EXTRACTION VESSEL EXPOSED



The extract solution was transferred to a tared flask and the solvent evaporated on a rotary evaporator at 40°C. After weighing the flask, the extract was transferred to a dish. The flask was rinsed with acetone:water (4:1) then the extract was dried overnight at 30°C in a vacuum oven. The dried extract was transferred to a glass vial for storage.

The procedure described above was modified for the replicate runs carried out to obtain extracts for chemical analysis and adhesives evaluation. The valve rinsings and extracts from the leak tests were discarded. At the end of each run the volume of extract solution was measured and an aliquot removed. The aliquot was dried overnight at 30°C in a vacuum oven and the yield calculated from the weight of extract. The remaining extract solution was combined with solutions previously obtained at the same experimental conditions. The combined solution was concentrated in a rotary evaporator at 30°C to one-tenth of its original volume then stored under nitrogen at 4°C. If required by a test method samples were dried overnight at 30°C in a vacuum oven.

The product yield was calculated from the weight of dried extract as a percentage of the weight of ovendry wood. The residue was weighed and the result expressed as a percentage of the weight of ovendry wood. The sum of the extract yield and the residue was expressed as the percent recovery. The difference between the percent recovery and 100 was assumed to be noncondensible gases.

Pretreatment of cedar sawdust with acid or alkali was carried out by adding the required chemical to the sawdust in a closed container and allowing the mixture to stand at room temperature for 3 days. The concentrated acids were added to

give a weight percent based on dry wood. Sodium hydroxide and calcium carbonate were added as 20% aqueous solutions to give a percentage by weight of reagent to weight of dry wood. Ammonia was added as concentrated ammonium hydroxide solution.

2.3 Analytical Methods

2.3.1 Ovendry Weight of Wood

Samples from each batch of wet wood were dried at 105°C for sixteen hours and the percent ovendry wood in the sample calculated.

2.3.2 Calorific Value

A Parr Adiabatic Calorimeter was used to determine the calorific value of the samples. Paraffin oil of known calorific value was added to the sample as a combustion aid.

2.3.3 Elemental Analysis

Analysis of the samples for carbon, hydrogen, nitrogen and oxygen was carried out by Canadian Microanalytical Services Ltd., Vancouver.

2.3.4 Thermogravimetric Analysis

Samples were analyzed for ash, volatiles and combustibles on a DuPont 1090 Thermal Analysis/Data System operating with a 951 Thermogravimetric Analyzer. The samples were heated in a flow of air from 25°C to 700°C.

2.3.5 Equivalent Weight

The equivalent weight was determined by titrating an aqueous solution of extract with 0.05N sodium hydroxide. A graph of pH against volume of sodium hydroxide added was drawn to locate the equivalence point.

2.3.6 Molecular Weight

The molecular weight was determined by vapour pressure osmometry using acetone as the solvent. The tests were carried out by Galbraith Laboratories, Knoxville, Tennessee.

2.3.7 Methoxyl Content

Methoxyl contents were determined by Galbraith Laboratories, Knoxville, Tennessee. The procedure used was ASTM D1166 (ASTM, 1981).

2.3.8 Specific Gravity

Specific gravity of extracts was determined by ASTM method D 70 (ASTM, 1981).

2.3.9 Thin Layer Chromatography

Samples were applied to precoated sheets of silica gel on aluminum, layer thickness 0.2 mm.

The developing solvents were:

1. 2-butanol:acetic acid:water, 4:1:1
2. benzene:ethyl acetate, 8:1.

The first solvent mixture separated the carbohydrate fraction from the phenolic fraction. The second mixture separated components of the phenolic fraction. Two dimensional chromatography was carried out using the first mixture followed by the second mixture.

The plate was sprayed with concentrated sulfuric acid and briefly heated at 105°C.

2.3.10 Gas Chromatography

The extracts were analyzed on a 12 m OV-101 capillary column. The injection temperature was 200°C and the flame ionization detector temperature was 300°C. An oven temperature of 50°C was used to study volatile compounds. To examine less volatile compounds the oven was held at 50°C for 4 minutes, programmed at 16°C/min to 250°C and held for 8 minutes. Cyclohexanone was added to the samples as an internal standard.

Analysis of the extracts for phenolic compounds by GC-MS was carried out by Weyerhaeuser Limited, Tacoma, Washington. A 30 m SE 54 (Durabond) capillary column was used at 50°C for 4 minutes, then programmed to 280°C at 16°C/min.

2.3.11 Determination of Levoglucosan

Qualitative analysis for levoglucosan in the extracts was carried out by thin layer chromatography. Extracts and levoglucosan were examined before and after acid hydrolysis by the procedure described in Section 2.3.9. The plates were developed with a mixture of 2-butanol:acetic acid: water, 4:1:1. Acid hydrolysis of the samples was carried out by adding 60 mg of sample or levoglucosan and 20 ml of 0.15 N

sulfuric acid to a test tube. The tube was placed in a boiling water bath for 32 hours. Barium carbonate was added to neutralize the acid, the sample filtered and water evaporated on a rotary evaporator. About 5 ml of methanol was added to the residue, the mixture filtered and made up to 10 ml with methanol (Wolfram, 1959).

Levoglucosan was determined quantitatively by acid hydrolysis of the extracts, acetylation of the products and analysis for glucose by gas chromatography. The sample, 1.8 g, was acid hydrolyzed as described above. After evaporation of methanol, acetylation was carried out by refluxing a mixture of the sample, 0.9 g of sodium acetate and 18 ml of acetic anhydride, for 2.5 hours. The mixture was poured into 200 ml ice water, stirred for 2.5 hours and allowed to stand overnight. The suspension was extracted three times with chloroform, total volume 70 ml. The chloroform was washed with 30 ml water and 30 ml sodium bicarbonate solution, dried with sodium sulfate, filtered and made up to 100 ml with chloroform (Wolfram, 1959). Analysis by gas chromatography was performed as described in Section 2.3.10.

2.4 Preparation and Evaluation of Plywood Adhesives

Phenol-formaldehyde adhesives were prepared with partial substitution of the phenolic resin by supercritical gas extracts. Two extracts were tested; a methanol and an acetone extract of Western red cedar, both prepared at 350°C and 10 MPa. The strength of the adhesive bond was measured on 3-ply plywood with 15% and 30% substitution of the resin. The procedures for preparing adhesive mixtures and plywood samples are described in Appendix A.

3.0 EQUIPMENT AND METHODS: LOW TEMPERATURE EXTRACTIONS

3.1 Equipment

The equipment shown in Figures 3 and 4 was used to extract chemicals from forest products using supercritical fluids which are gaseous at ambient temperatures. A 76 MPa double-ended, motordriven diaphragm compressor (Superpressure) was controlled by a meter (Superpressure) which was located between the compressor and the base of a Kuentzel extraction vessel (Autoclave Engineers). The top of the extraction vessel was connected to a valve (Superpressure). The low pressure outlet of the valve was connected to a glass U-tube containing a plug of glass wool in the exit arm. The collection tube was cooled in a bath containing acetone and dry ice. The volume of gas leaving the U-tube was measured by a gas meter (Canadian meter) and the flow measured with a flow meter (Matheson). The sample and gas were heated in a water bath which was maintained at the experimental temperature by an immersion heater (Brinkmann).

Extractions with propane (T_c, 96.8°C) were carried out using the equipment described in Section 2.1 for high temperature studies. An ice bath was used to cool the collection tube.

3.2 Operating Procedure

The extraction vessel was filled with 30 to 40 grams of lightly compacted wet sample. The vessel was placed in the water bath and the system pressurized to the experimental pressure. After thirty minutes the valve was opened to give a gas flow of about 6 litres per minute. The gas flow and volume were measured at room temperature. After the required

Figure 3

SUPERCRITICAL GAS EXTRACTION APPARATUS EMPLOYING FLUIDS
WHICH ARE GASEOUS AT AMBIENT TEMPERATURE

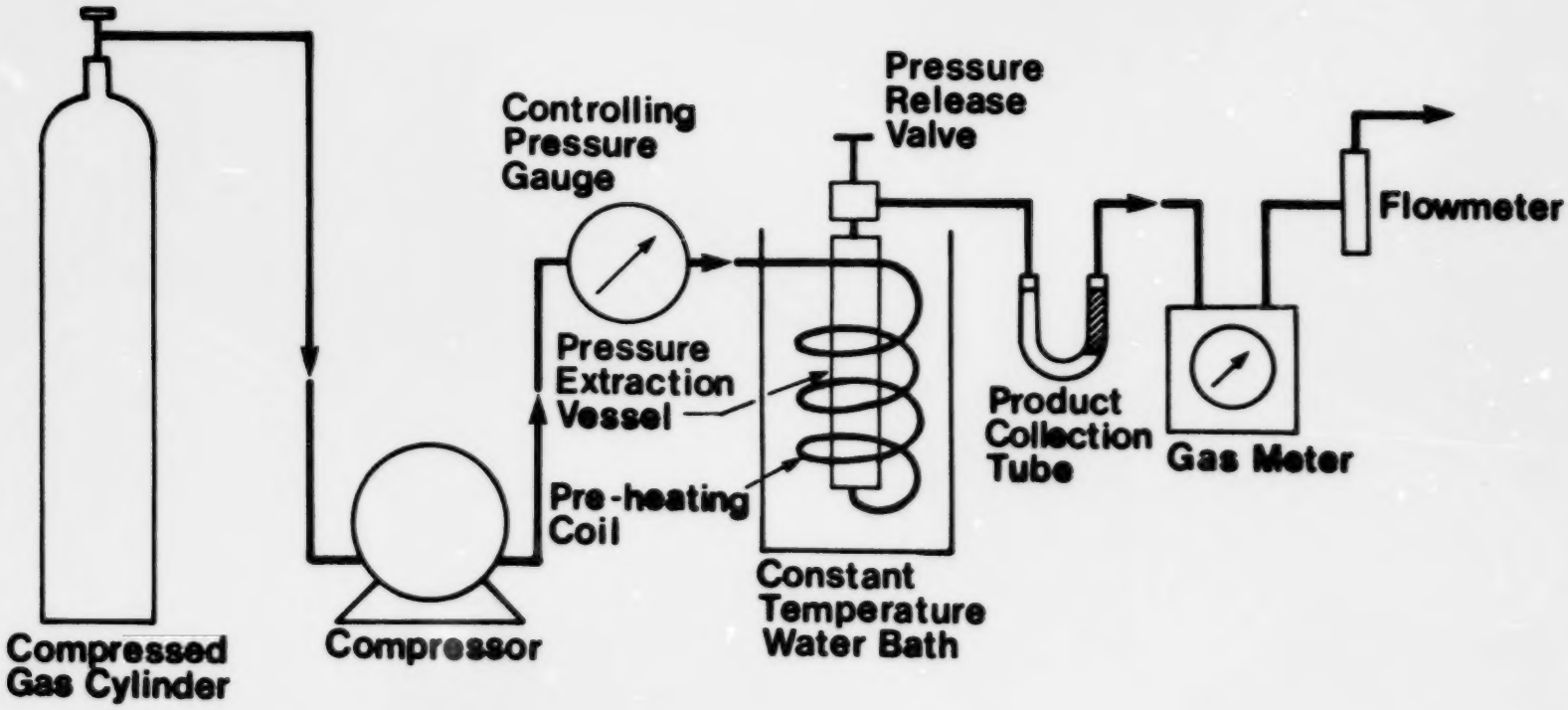
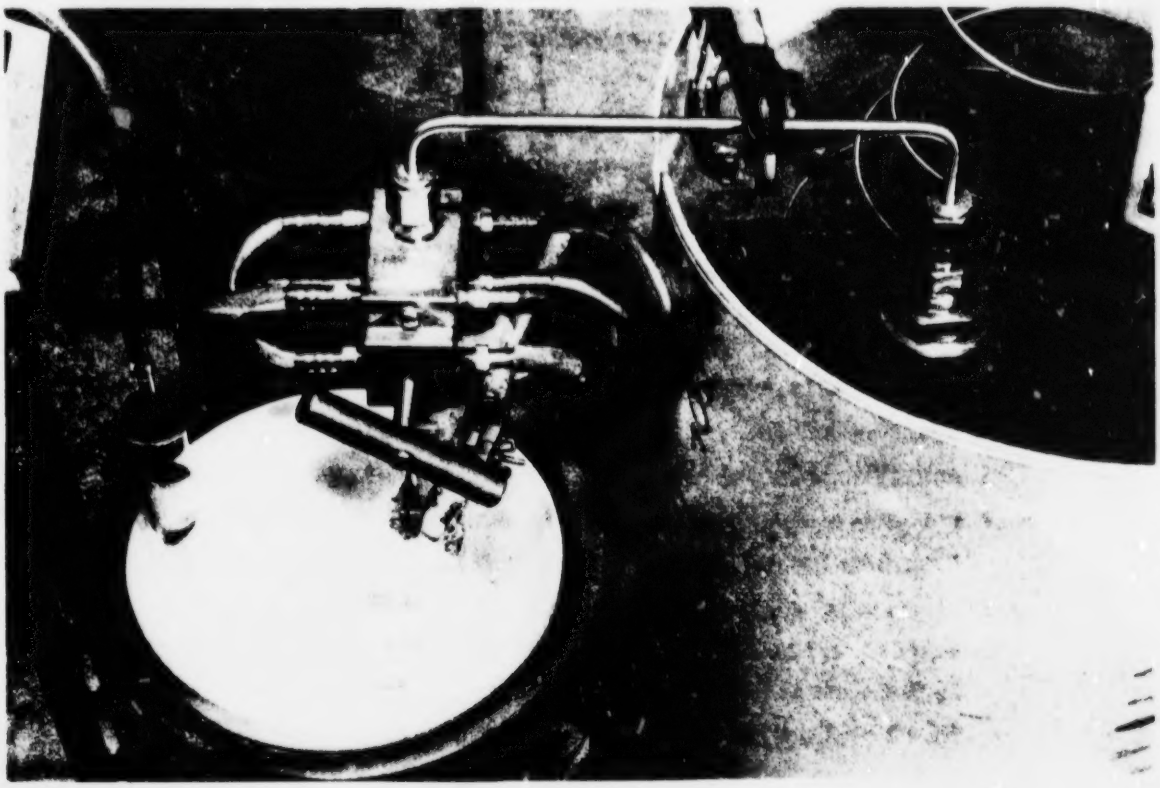


Figure 4 (24465.15A)

LOW TEMPERATURE SUPERCRITICAL GAS EXTRACTION OF WOOD: EXTRACTION VESSEL AND PRODUCT COLLECTION TUBE



volume of gas had passed through the sample the pressure was released. The collection tube was changed three or four times during some of the experiments.

Propane extractions were carried out as described above using the fluidized sand bath instead of the water bath. The flow rate was 5 millilitres per minute, the highest flow rate of the pump. The maximum pressure of the pump was 34 MPa, precluding propane extractions above this pressure.

Pine extracts were dissolved in a mixture of methanol and petroleum ether (4:1). An aliquot of the solution was dried overnight in a vacuum oven at 30°C and the yield calculated from the weight of extract. Sodium sulfate was added to the remaining solution before storing at 4°C.

Wax extracts were removed from the collection tube using a spatula and the yield calculated by weighing the tube before and after removal of the extract. A mixture of ethyl acetate and petroleum ether (9:1) was used to dissolve the wax when required for analysis.

Soxhlet extractions were run with 4 to 10 g of sample in 25 x 80 mm thimbles. About 6 cycles per hour were used for 6 to 40 hours with a solvent volume of 120 to 150 ml. The extract was made up to a final volume of 200 ml. Yields were calculated after drying an aliquot of the extract solution overnight in a vacuum oven at 30°C.

Extract yields were calculated as a percentage of ovendry wood or bark.

3.3 Analytical Methods

3.3.1 Ovendry Weight of Wood

Samples of wood and bark were dried at 105°C for sixteen hours and the percent ovendry sample calculated.

3.3.2 Melting Point

The melting point ranges of wax extracts were determined on a Thomas Model 40 Micro Hot Stage.

3.3.3 Saponification of Waxes

The saponification numbers of wax extracts were found by the procedure described in ASTM D1387 (ASTM, 1981).

The same procedure was used to saponify wax extracts for gas chromatography but the titration was omitted. After refluxing for 3 hours the solution was cooled and acidified to pH 3 with 20% sulfuric acid solution. Water was evaporated and the residue washed with 80 ml diethyl ether. The ether was filtered into a 100 ml volumetric flask and made up to volume with ether.

3.3.4 Saponification of Resin and Fatty Acids

The procedure described in ASTM D464 was used to saponify the resin acid solutions but the titration was omitted (ASTM, 1981). After boiling the solution for 1 hour, it was cooled and acidified to pH 3 with 0.5 N sulfuric acid. The solution was evaporated to about 1 ml, 5 ml of methanol added and the evaporation to 1 ml repeated. Sodium sulfate was added and the residue washed with 8 ml of methanol. The methanol solution was filtered into a 10 ml volumetric flask and made up to volume.

3.3.5 Gas Chromatography

Analyses for turpentine, fatty acids, resin acids and waxes were carried out on a 12 m OV-101 capillary column. Turpentine was analyzed with an oven temperature of 80°C. Fatty acids, resin acids and waxes were analyzed with the oven temperature programmed from 190°C to 250°C; 10 minutes at 1°C/min, 10 minutes at 2°C/min and 10 minutes at 3°C/min. The samples were methylated before injection (Chung, 1979).

GC-MS of the wax samples was run by CANTEST Limited, Vancouver.

3.3.6 Thin Layer Chromatography

Hemlock extracts and conidendrin were applied to precoated sheets of silica gel on aluminum, layer thickness 0.2 mm. Plates were developed with a mixture of 2-butanol:acetic acid:water (4:1:1) then sprayed with a mixture of 1 volume 5% aqueous potassium ferricyanide, 2 volumes 10% aqueous ferric chloride and 8 volumes water.

4.0 RESULTS AND DISCUSSION: HIGH TEMPERATURE EXTRACTIONS

The work presented in this report was carried out to achieve two main goals. First, chemical characterization of supercritical gas extracts obtained using extraction conditions determined by an economic analysis of the process. Second, an evaluation of extracts as substitutes for phenol in phenolic resins used for plywood manufacture.

Experiments were previously carried out to study the effect on product yield of varying the time, flow rate, solvent type, wood species and the effect of acid pretreatment of wood. The results of this work have been discussed in a previous ENFOR report (McDonald, 1981). Some of these results are repeated in this report for comparison with recent work.

The following is a brief summary of the effects of the variables listed above on product yield.

1) Extraction time and flow rate did not have a large effect on yield. At 260°C the yield increased with longer extraction time but at 360°C time and flow rate had minimal influence on yield.

2) Methanol, acetone, toluene and water were studied. The first two solvents gave the highest yields at temperatures and pressures close to their critical values (260°C and 10 MPa).

3) Softwood species, Western red cedar and hemlock, gave higher yields than a hardwood, red alder, at 260°C and 10 MPa. However, the yields for all three species were in excess of 70%, based on dry wood, at 360°C and 28 MPa.

4) Acid pretreatment of Western red cedar gave a yield with acetone of 73% at 260°C and 10 MPa compared to a yield of 36% obtained from untreated wood.

All product and residue yields quoted in the discussion are expressed as a percentage of dry wood in the sample.

4.1 Effect of Temperature and Pressure on Product Yield

The results reported last year on the effect of varying temperature and pressure on product yields using methanol were obtained with a cedar sawdust sample which had been contaminated by acid fumes during a laboratory fire. Product yields were higher with the contaminated sawdust than those obtained from uncontaminated sawdust. Runs were repeated using a fresh batch of cedar sawdust at a pressure of 10 MPa.

Figure 5 and Table 1 show the change in yield for methanol and acetone extracts with a temperature increase from 260°C to 360°C. The results for acetone extractions are those reported last year (McDonald, 1981). The yield obtained with methanol increased linearly from 20% at 260°C to 42% at 360°C. Acetone gave higher yields than methanol at the temperatures studied, for example, 35% using acetone and 20% using methanol at 260°C. The yield with acetone increased more rapidly between 260°C and 310°C than the methanol yields, then remained constant at 53% from 310°C to 360°C.

Figure 6 and Table 2 show that increasing the extraction pressure gave an increase in product yield. Yields obtained with methanol increased from 42% at 10 MPa, to 70% at 28 MPa. Acetone gave yields of 55% at 10 MPa and 74% at 28

Figure 5

SUPERCRITICAL GAS EXTRACTION OF CEDAR: EFFECT OF TEMPERATURE ON PRODUCT YIELD (10 MPa, 5.6 ml/min, 60 min)

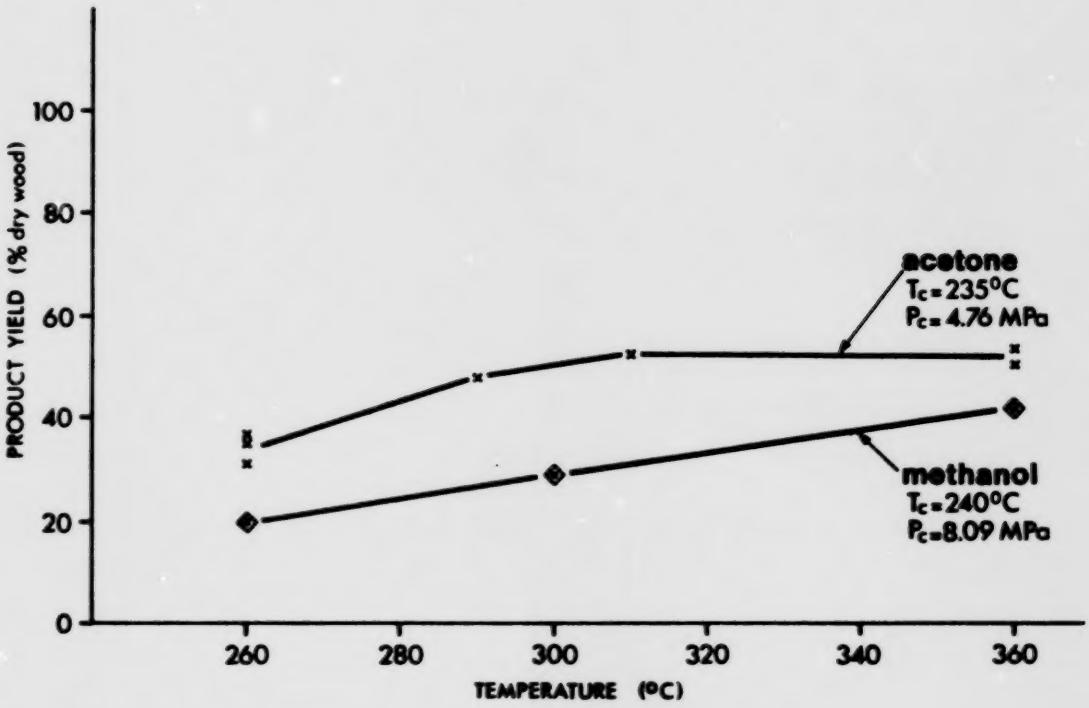


TABLE 1

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
EFFECT OF TEMPERATURE ON PRODUCT YIELD

Solvent	Temperature °C	Pressure MPa	Product Yield % dry wood	Residue %	Recovery %
Methanol	360	10	42	28	70
	300	10	30	48	78
	260	10	20	72	92
Acetone	360	10	53	25	78
	310	10	53	27	80
	290	10	48	37	85
	260	10	35	59	94

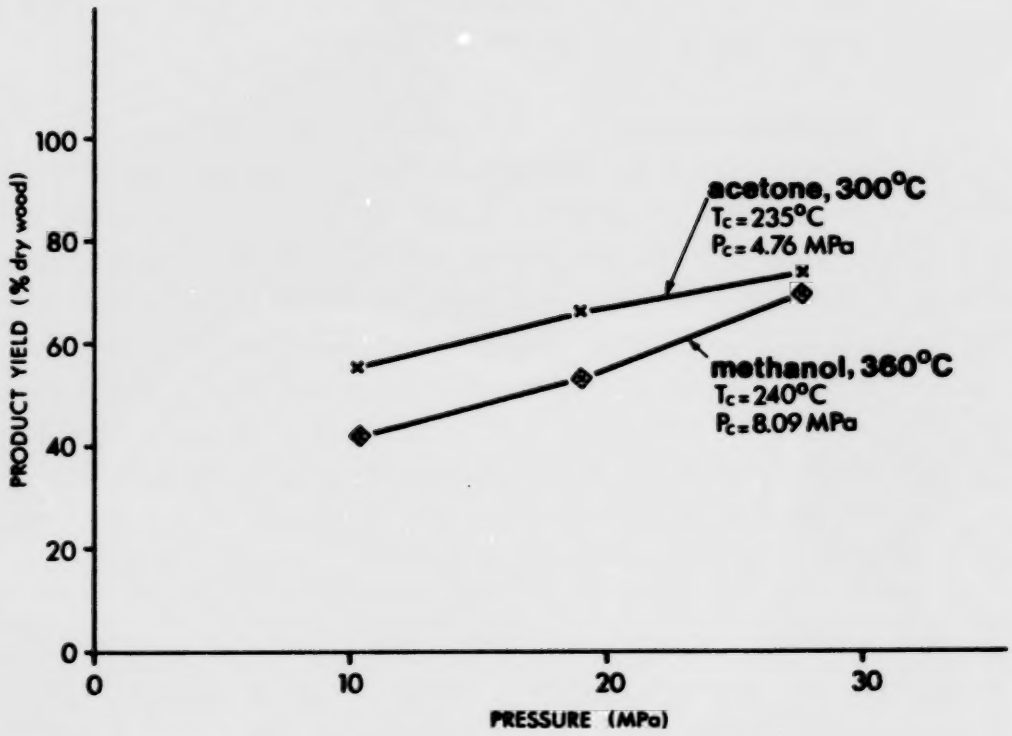
TABLE 2

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
EFFECT OF PRESSURE ON PRODUCT YIELD

Solvent	Pressure MPa	Temperature °C	Product Yield % dry wood	Residue %	Recovery %
Methanol	10	360	42	28	70
	19	360	53	14	67
	28	360	70	4	74
Acetone	10	300	55	29	84
	19	300	66	15	81
	28	300	74	9	83

Figure 6

**SUPERCRITICAL GAS EXTRACTION OF CEDAR:
EFFECT OF PRESSURE ON PRODUCT YIELD
(5.6 ml/min, 60 min)**



MPa. The extraction temperature for these experiments was chosen from the results shown in Figure 5. Acetone yields had not increased at temperatures above 300°C while those of methanol had increased linearly up to 360°C.

The 74% yield of product extracted by acetone at 300°C and 28 MPa represents 89% of the theoretical yield, assuming that acetone had not reacted with the cedar sawdust. The charge of wet wood was 30 g. This was equivalent to 13 g of ovendry wood with a carbon content of 50%, which gave 6.5 g of carbon in the wood. The extract weighed 9.5 g with a carbon content of 61% equivalent to 5.8 g of carbon. Therefore, the carbon content of the extract was 89% of the carbon available in the wood.

The yield obtained with acetone was greater than with methanol at any given temperature and pressure. The critical temperatures of acetone and methanol are similar but the critical pressure of acetone, 4.76 MPa, is lower than that of methanol, 8.09 MPa. Therefore, the ratio of extraction pressure to critical pressure was greater for acetone than methanol. For example, at 10 MPa the ratio for acetone was 2.1 and for methanol 1.2. This difference in pressure ratios may be a factor in the higher yields obtained with acetone.

4.2 Pretreatment of Wood with Acid or Alkali

Table 3 shows the effect on product yield of adding either acid or alkali to cedar sawdust. When acetone was the supercritical gas, at 260°C and 10 MPa, the product yield increased from 36% to 47% with the addition of 0.4% w/w hydrochloric acid. The yield increased to 73% with the addition of 10% w/w hydrochloric acid. To obtain a yield of 73% without acid pretreatment would require a pressure of 28 MPa and a temperature of 360°C. The increase in yield with the addition of 0.4% hydrochloric acid indicates that a yield in excess of 70% could probably be achieved with an addition of about 2% acid.

Acetic acid pretreatment was not as effective as hydrochloric acid. A yield of 41% was obtained with 1% w/w acetic acid, compared to 47% with 0.4% hydrochloric acid.

Without pretreatment of the wood, methanol at 260°C and 10 MPa gave a yield of 20%. Addition of 10% w/w hydrochloric acid gave a yield of 60 percent. The addition of 5% w/w sodium hydroxide increased the yield to 34% from 20% with untreated wood. Increasing the amount of sodium hydroxide to 10% gave no further increase in yield. Calcium carbonate gave a smaller increase in yield than sodium hydroxide and ammonia reduced the yield below that of the untreated wood (Law, 1982).

These data show that pretreatment of the wood with acid has a greater effect on product yield than pretreatment with alkali. Investigation of acid or alkali pretreatment of wood as potential pulping techniques, by analysis of the lignin-to-carbohydrate ratio in the residues, was not carried out.

TABLE 3

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
EFFECT ON PRODUCT YIELD OF ACID OR
ALKALI PRETREATMENT OF WOOD
(260°C, 10 MPa)

Solvent	Pretreatment % w/w on dry wood	Product Yield % dry wood	Residue %	Recovery %
Acetone	None	36	53	89
	1% w/w glacial acetic acid	41	30	71
	0.4% w/w conc. HCl	47	27	74
	10% w/w conc. HCl	73	18	91
Methanol	None	20	72	92
	10% w/w conc. HCl	60	50	110
	5% w/w NaOH	34	65	99
	10% w/w NaOH	32	67	99
	5% w/w $CaCO_3$	25	66	91
	5% w/w NH_3	16	76	92

4.3 Preparation of Extracts and Statistical Analysis of Product Yields

Supercritical gas extracts were prepared for chemical analysis and evaluation in adhesive formulations. Three extracts were prepared using acetone at 350°C, acetone at 260°C and methanol at 350°C, all runs at a pressure of 10 MPa, flow rate of 4 ml/min and extraction time of 30 minutes. Replicate extractions were required to produce sufficient extract for analysis.

Statistical analysis of the product and residue yields from these replicate runs is shown in Table 4. The standard deviation of the product yields was between 2 and 2.5% and was independent of extraction conditions.

The acetone yield at 260°C agreed with the yields obtained in previous extractions under the same conditions (Table 1), but the acetone and methanol yields at 350°C were lower (Tables 1 and 4). The percent residue from the acetone runs at 350°C was similar to that obtained in previous runs, while the residue from the methanol runs was higher than that obtained in recent work. Examination of the sawdust, solvents and equipment did not find the cause of these lower yields. A problem with the bath thermocouple, a few months later, indicated that the measured temperature of 350°C may have been closer to 335°C. However, a lower extraction temperature may explain the higher residue results but does not explain the significantly lower product yields. Figure 5 showed that the acetone yield did not change at temperatures between 310 and 360°C. The drying technique for calculation of the yield was considered as a possible cause of error.

TABLE 4

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
STATISTICAL ANALYSIS OF PRODUCT YIELDS

Extraction Solvent and Temperature[a]	No. of Runs	Product Wt. % Dry Wood		Residue Wt. % Dry Wood	
		Mean	Standard Deviation	Mean	Standard Deviation
Acetone, 350°C	21	33.8	2.5	31.9	1.2
Acetone, 260°C	6	33.7	2.5	56.7	5.0
Methanol, 350°C	10	26.1	2.1	36.6	3.0
Acetone, 360°C (1980 results)	4	52.9	-	27.3	-
Methanol, 360°C (1982 results)	2	41.9	-	28.2	-

[a] Pressure 10 MPa, flow rate 4 ml/min., time 30 min.

In two experiments, product yields determined by drying an aliquot of the extract solution in a vacuum oven were lower than the yields obtained when the solvent was evaporated from the total extract solution in a rotary evaporator. However, in all subsequent experiments these differences in yield did not occur between the two drying techniques. In conclusion, a satisfactory explanation has not been found for the low product yields obtained using acetone and methanol at 350°C.

4.4 Analysis of Residues and Feed

The appearance of the residues obtained at 350°C indicated little or no char formation. The residue at 260°C looked like the original wood.

Table 5 shows the elemental analysis, ash, calorific value and percent combustibles of Western red cedar sawdust, and residues after extraction with acetone and methanol. Thermogravimetric analysis scans are included as Appendix B.

The acetone residue at 260°C and the cedar sawdust had similar carbon, hydrogen and oxygen contents, ashes and calorific values, indicating that the overall composition of the wood was essentially unchanged. The residue was 57% of the original wood (Table 4). Therefore, 43% of the wood was degraded to produce liquid extract and noncondensible gases. The extractives and hemicelluloses in Western red cedar amount to only 23% (Barton, 1971). Consequently, lignin and/or carbohydrates have been degraded also. Reference to previous work on the extraction of hemlock with methanol indicated that both lignin and carbohydrates are degraded at 260°C (Howard, 1980). Table 6 shows that lignin was present in the residue (21%). Carbohydrate analysis showed that sugars were still present in the residue in significant amounts.

TABLE 5

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
ELEMENTAL ANALYSIS, ASH AND CALORIFIC VALUE
OF RESIDUES AND FEED

Parameter	Feed	Residue		
		Acetone 350°C	Acetone 260°C	Methanol 350°C
C, wt. %	50.21	73.19	52.16	71.04
H, wt. %	6.30	5.01	6.00	5.53
N, wt. %	0.08	0.12	0.07	0.10
O, wt. %	40.30	18.51	37.98	21.38
H/C ratio, atomic	1.51	0.82	1.38	0.93
Ash, wt. % dry basis[a]	0.19	1.8	0.04	1.7
Calorific value, kJ/kg	19,700	30,200	17,200	25,600
Combustibles[a] wt. % dry basis	99.8	98.1	99.7	98.3

[a] thermogravimetric analysis

TABLE 6

SUPERCRITICAL GAS EXTRACTION OF HEMLOCK:
CARBOHYDRATE AND LIGNIN ANALYSIS ON WOOD AND RESIDUE

Description of Sample	Elemental Analysis (%)			Carbohydrate Analysis (%)					Klason Lignin (%)	A/B[c] Solubles (%)	Calorific Value (kJ/kg)
	C	H	O[a]	Galactose	Mannose	Arabinose	Xylose	Glucose[b]			
Hemlock Wood	48.31	6.29	45.40	2.2	12.7	1.2	3.4	45.79	32.5	2.31	19,300
Residue from Methanol Extraction at 260°C & 21MPa	47.29	5.92	46.79	0.8	10.6	0.1	3.0	59.9	20.6	5.00	18,500

a to 100%

b to 100% including Klason Lignin and A/B Solubles

c alcohol:benzene, 1:2

At 350°C the residues from acetone and methanol extractions had higher carbon and lower hydrogen values than the feed with carbon contents of 73 and 71% compared to 50% in the sawdust. The calorific value of 25,600 kJ/kg for the methanol residue was lower than that for the acetone residue of 30,200 kJ/kg, as a result of the higher oxygen content in the methanol residue.

The ash contents of the residues obtained at 350°C are higher than expected. For example, if ash in the sawdust remained entirely in the residue, the calculated ash content of the acetone extract would be 0.6%, whereas the measured value was 1.8%.

4.5 Analysis of Supercritical Gas Extracts

The analyses reported in this section were carried out on three extracts of Western red cedar sawdust. The extraction conditions were: acetone at 350°C, acetone at 260°C and methanol at 350°C, all at a pressure of 10 MPa. A number of extractions was required at each of the three conditions to obtain sufficient extract for analysis and for adhesives evaluation discussed in section 4.7.

4.5.1 Elemental Analysis, Ash and Calorific Value

Table 7 shows the analysis of products for elements, calorific value, specific gravity, ash, volatiles and combustibles. The last three items were obtained by thermogravimetric analysis. The scans are included in Appendix B.

TABLE 7

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
ELEMENTAL ANALYSIS, ASH AND
CALORIFIC VALUE OF PRODUCTS

Parameter	Extraction Solvent and Temperature		
	Acetone 350°C	Acetone 260°C	Methanol 350°C
C, wt. %	58.19	58.97	55.70
H, wt. %	6.94	6.69	6.84
N, wt. %	0.09	0.09	0.11
O, wt. %	33.81	33.39	36.31
H/C ratio, atomic	1.43	1.36	1.47
Ash, wt. % dry basis	0.88	0.26	1.01
Calorific value, kJ/kg	25,600	-[a]	24,400
Volatiles, wt. % dry basis[b]	70.5	56.6	72.1
Combustibles wt. % dry basis[b]	27.8	43.2	26.0
Specific gravity, g/ml	1.26	-[a]	1.24

[a] insufficient sample for analysis
[b] thermogravimetric analysis

The carbon content of the methanol extract is lower than those of the acetone extracts, while the oxygen content is higher. This is due to a high methoxyl content in the methanol extract compared to the acetone extracts (refer to Section 4.5.2). The H/C ratios of about 1.4 are similar to that of the feed, 1.51. The calorific values are similar for the acetone and methanol extracts at 350°C; 25,600 and 24,400 kJ/kg, respectively. Insufficient sample was available for determination of the calorific value on the acetone extract at 260°C.

By comparison with the feed (Table 5), the acetone product (Table 7) had a lower oxygen content and a higher calorific value. However, the H/C ratio for the acetone product was less than that for the feed. These data indicate that the product was not upgraded significantly compared to the feed and would not be marketable as a liquid fuel. Further processing of the products would be required to produce a marketable commodity.

Thermogravimetric analysis showed two distinct zones as the extracts were heated. Between 25°C and 500°C volatile material was driven off (% volatiles) then the remaining extract ignited (% combustibles). The acetone extract at 260°C had a lower percentage of volatile material (57%) than the extracts at 350°C (71-72%), indicating that the molecular weights of the extracted materials were greater at the lower temperature than at 350°C.

Specific gravities of the acetone and methanol extracts were 1.26 and 1.24 g/ml respectively. Ash contents of the acetone and methanol extracts at 350°C were 0.9 and 1.0%, about four times greater than the ash content of the extract at 260°C.

4.5.2 Methoxyl Content and Equivalent Weight

Methoxyl contents of the extracts, residues and sawdust are shown in Table 8. The higher methoxyl content found in the methanol residue than in the feed indicates that methanol had reacted with the sawdust. The methanol extract and residue have methoxyl contents almost double those obtained with acetone. If the methoxyl results for the acetone extract and residue are assumed to be representative of no reaction between solvent and feed, then the methanol consumed by reaction would be 5% by weight of dry feed[(1)]. Economic analysis of the process has shown a loss of this magnitude to be unacceptable.

The equivalent weight for the methanol extract, 1980, was about five times the equivalent weights of the acetone extracts. Therefore, fewer acidic hydroxyls are available in the methanol extract for crosslinking reactions when extracts are used as substitutes for phenol in phenolic resins.

Molecular weights of the extracts, measured by vapour pressure osmometry, were lower than the equivalent weights. The procedure appeared to have measured only the volatile fraction of the extracts. Therefore, the procedure was not appropriate for these samples. Size exclusion chromatography would possibly be a better procedure for the determination of molecular weights.

---

(1) Methanol loss, assuming 100g dry feed, 30% yield, 40% residue, % methoxyl from Table 8;

Residue (40 X 0.130) - (40 X 0.063) = 2.7g
Extract (30 X 0.154) - (30 X 0.081) = 2.2g
Total methanol loss = 4.9g/100g dry feed

TABLE 8

SUPERCRITICAL GAS EXTRACTON OF CEDAR:
METHOXYL CONTENT AND EQUIVALENT WEIGHT OF FEED,
PRODUCTS AND RESIDUES

	Methoxyl Content % dry basis	Equivalent Weight
Cedar Sawdust	7.77	-
Acetone, 350°C		
Product	8.05	397
Residue	6.33	-
Acetone, 260°C		
Product	8.90	426
Residue	6.32	-
Methanol, 350°C		
Product	15.36	1,980
Residue	12.99	-

4.5.3 Determination of Levoglucosan

Figure 7 shows a thin layer chromatogram of levoglucosan (1,6-anhydro-β-D-glucopyranose) before and after acid hydrolysis. Figure 8 shows chromatograms for acetone and methanol extracts before and after acid hydrolysis. Glucose was not found in the extracts before acid hydrolysis by either thin layer or gas chromatography. The average Rf value of the spot in the extracts was 0.53 compared to 0.57 for levoglucosan. After acid hydrolysis, the Rf value of the extract spot was 0.40 compared to 0.39 for glucose.

Quantitative analysis for levoglucosan was carried out by acetylating the acid hydrolyzed extracts and analyzing for acetylated glucose by gas chromatography. The results obtained were:

1) 1.6% by weight of methanol extract,
2) 1.9% of the acetone (350°C) extract,
3) 2.6% of the acetone (260°C) extract.

The lower results at the higher temperature indicate that levoglucosan has undergone secondary reactions, as found in previous studies (Wolfram, 1968). An investigaton of the thermal degradation of cellulose using supercritical acetone found the main component of the extracted syrup to be 39% levoglucosan, based on consumed cellulose (Köll, 1978). The lower quantities observed in our extracts compared to those from pure cellulose may be due to the presence of lignin, hemicelluloses and numerous other wood components. Similar reductions in levoglucosan yields were found when wood rather than pure cellulose was pyrolyzed under vacuum (Shafizadeh, 1979).

Figure 7 (24424.2)

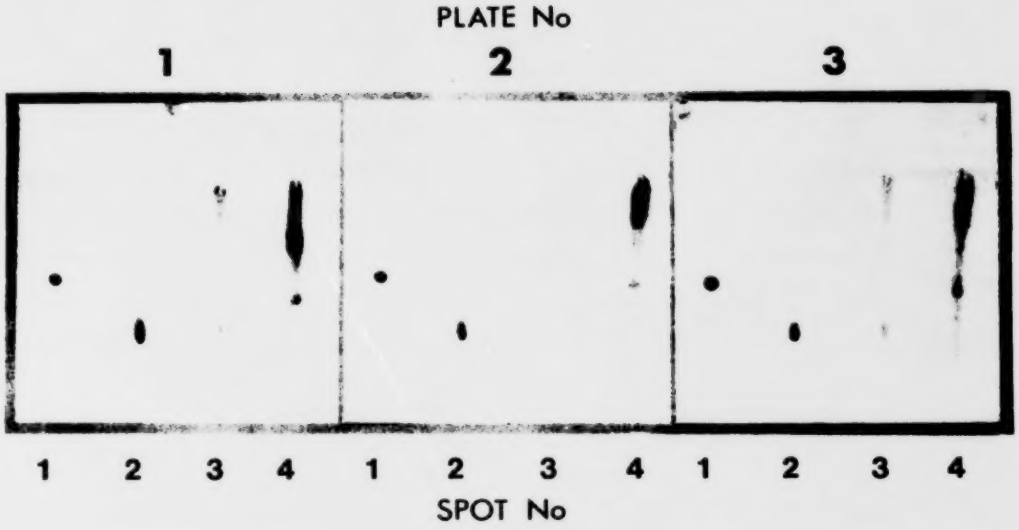
THIN LAYER CHROMATOGRAM OF LEVOGLUCOSAN BEFORE AND AFTER ACID HYDROLYSIS

SPOT No 1	LEVOGLUCOSAN
SPOT No 2	ACID HYDROLYSED LEVOGLUCOSAN
SPOT No 3	GLUCOSE
SPOT No 4	ACID HYDROLYSED GLUCOSE

Figure 8 (24424.11)

THIN LAYER CHROMATOGRAMS OF EXTRACTS BEFORE AND AFTER ACID HYDROLYSIS

PLATE No **1** ACETONE EXTRACT, 350°C, 10 MPa
PLATE No **2** ACETONE EXTRACT, 260°C, 10 MPa
PLATE No **3** METHANOL EXTRACT, 350°C, 10 MPa



SPOT No 1 LEVOGLUCOSAN
SPOT No 2 GLUCOSE
SPOT No 3 ACID HYDROLYSED EXTRACT
SPOT No 4 EXTRACT

4.5.4 Determination of phenols

Phenolic compounds present in the acetone and methanol extracts were determined by gas chromatography and mass spectrometry. The gas chromatograms of the extracts, Figures 9, 10 and 11, show that many volatile compounds are present. Most of the major peaks are present in all three chromatograms, with the exceptions of the following unidentified compounds; peak 2 in methanol extract only, peak 3 in acetone (260°C) only, peaks 4 and 5 not present in methanol extract. The compounds labelled 1 to 10 could not be matched to available reference mass spectra.

The benzenediol, shown in the extract chromatograms, is most likely hydroquinone added during preparation of the extracts as a free radical trapping agent to prevent polymerization. Examination of the extracts by thin layer chromatography, as the solvent and water were evaporated, indicated that addition of hydroquinone was not necessary if the extracts were dried at a temperature less than 40°C.

Table 9 shows the amounts of the identified phenols as a percentage of the extract. The total amount of extract identified was 2.3% for the acetone extracts and 3.0% for the methanol extract. The phenolic compounds are present in the extracts in different proportions but no pattern is evident showing that either the solvent or temperature had an effect on the substitution of the phenol. Both acetone extracts contained 4-ethylguaiacol as the major component, whereas guaiacol was the major component of the methanol extract. The low phenolic content of the extracts indicates that further processing would be required to upgrade the extracts before marketable commodities would be obtained.

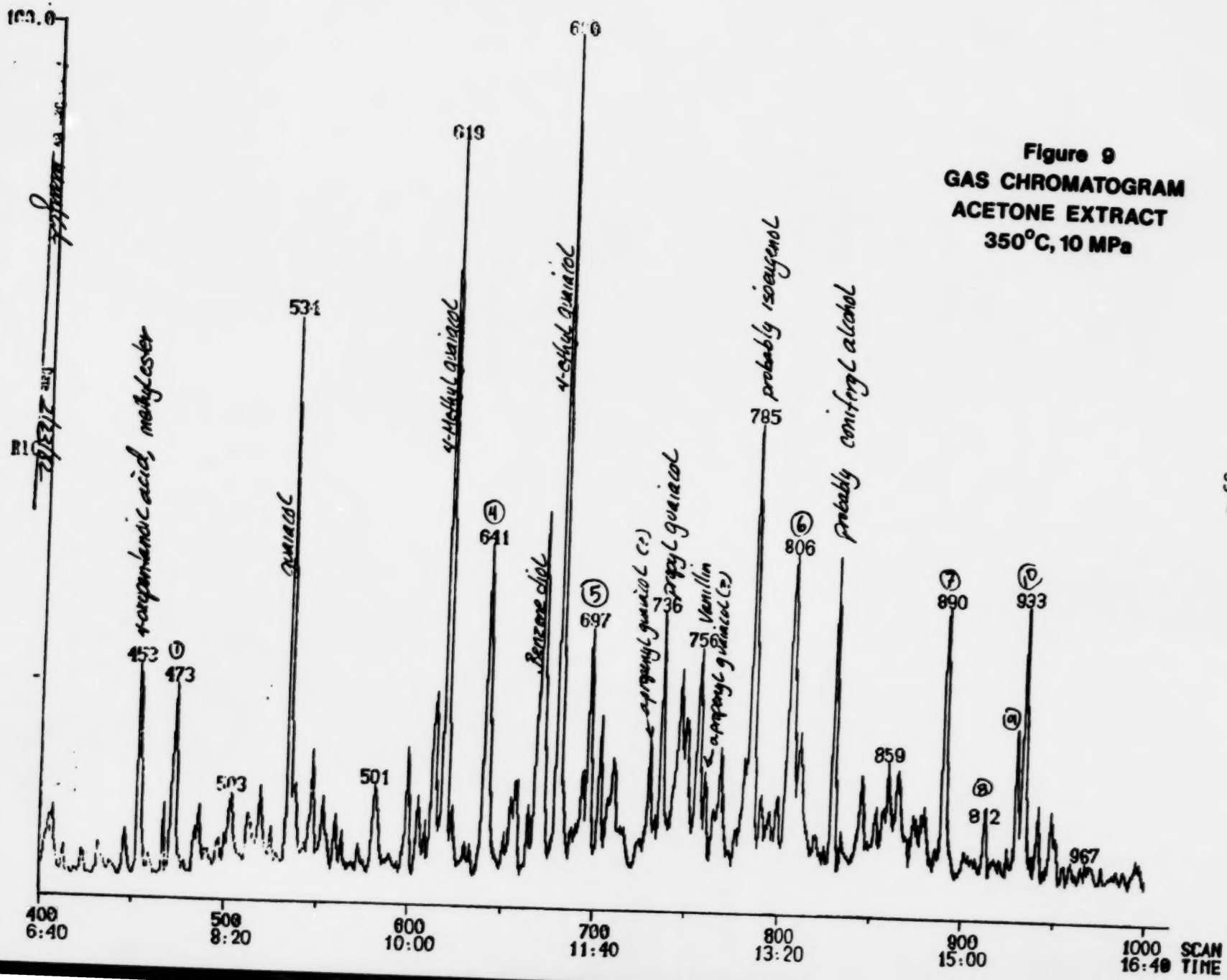


Figure 9
GAS CHROMATOGRAM
ACETONE EXTRACT
350°C, 10 MPa

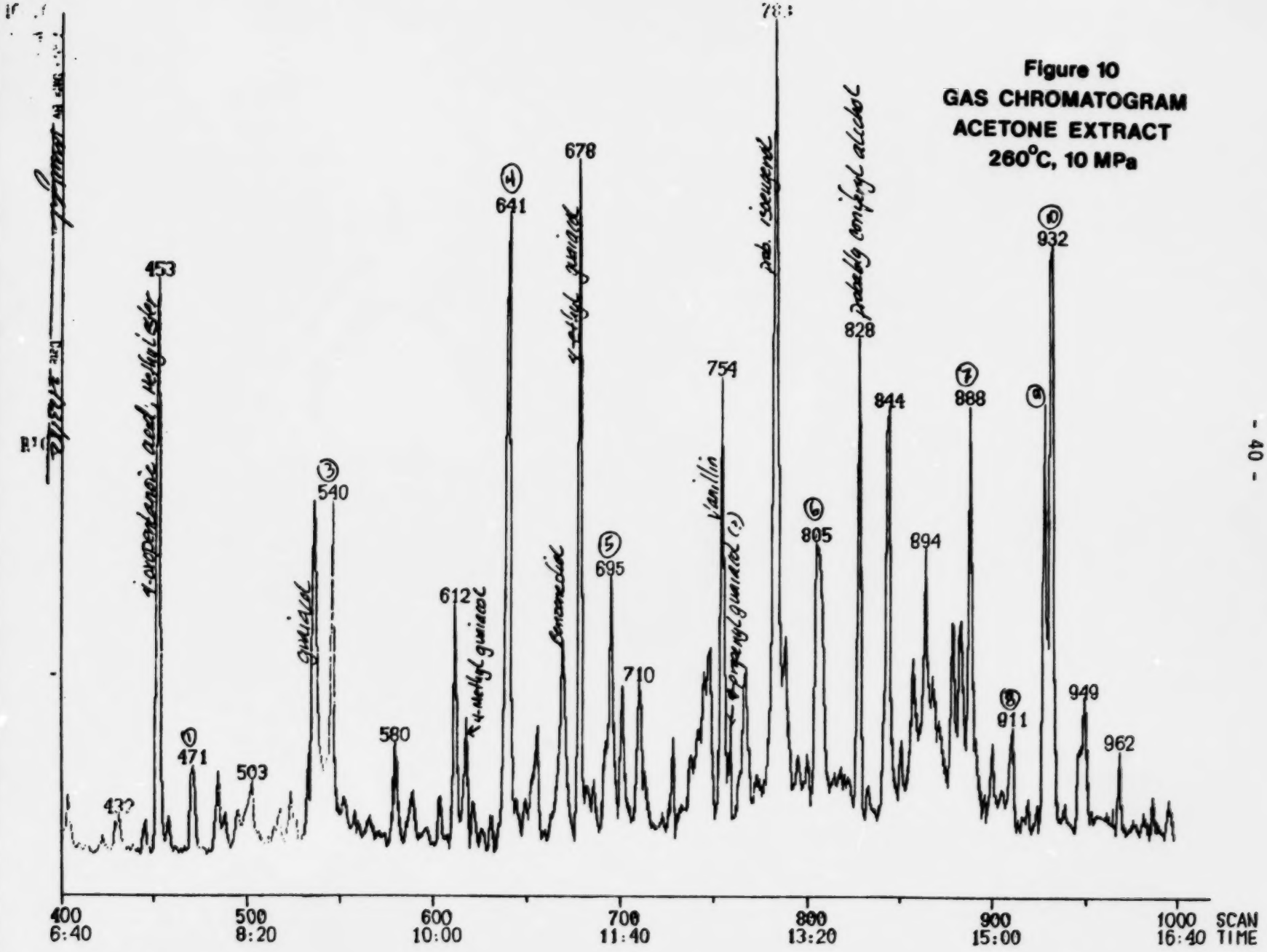


Figure 10
GAS CHROMATOGRAM
ACETONE EXTRACT
260°C, 10 MPa
453
471
503
540
580
612
641
678
695
710
754
805
828
844
888
894
911
932
949
962
400
6:40
500
8:20
600
10:00
700
11:40
800
13:20
900
15:00
1000
16:40
SCAN
TIME

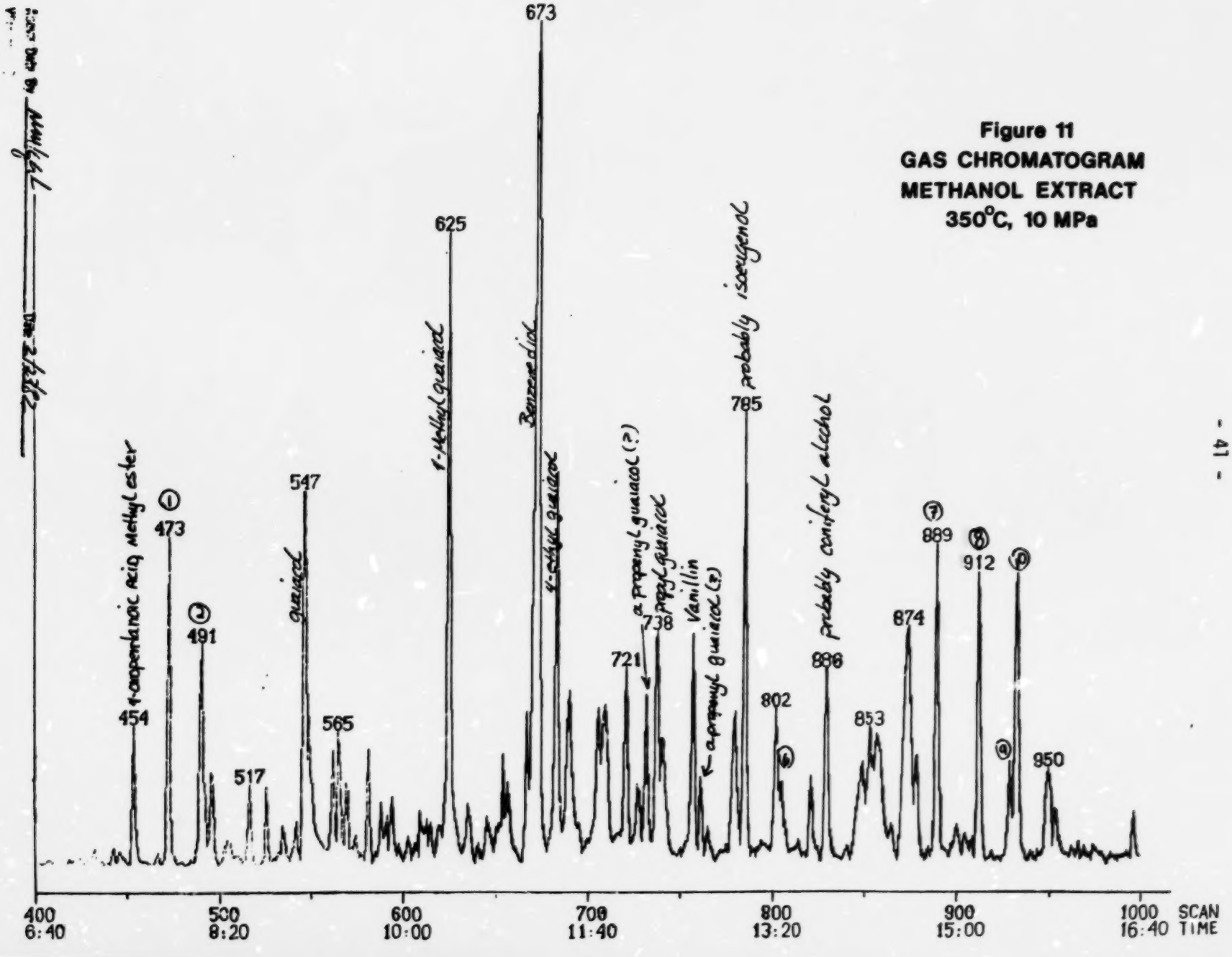


Figure 11
GAS CHROMATOGRAM
METHANOL EXTRACT
350°C, 10 MPa

TABLE 9

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
PHENOLIC COMPOUNDS PRESENT IN ACETONE
AND METHANOL EXTRACTS

Compound	Concentration, % of Extract		
	Acetone (350°C)	Acetone (260°C)	Methanol (350°C)
guaiacol	0.31	0.05	0.82
4-methylguaiacol	0.35	0.03	0.12
4-ethylguaiacol	0.59	1.09	0.18
4-n-propylguaiacol	0.17	ND[a]	0.54
vanillin	0.31	0.49	0.56
isoeugenol[b]	0.23	0.19	0.37
coniferyl alcohol[b]	0.31	0.40	0.43
TOTAL	2.27	2.25	3.02

[a] not detected
[b] tentatively identified

The phenolic content of an acetone extract of spruce wood, at 260°C and 8 MPa was examined (Calimli, 1978). While there was some difficulty in translating these results to compare with the results shown in Table 9, it appears that the listed compounds were present as 15% of the spruce wood extract.

4.6 Analysis of Recovered Solvent

After completing the replicate series of extractions, the volume of each extract was reduced to one-tenth of the initial volume and the collected solvent examined by gas chromatography. Figure 12 shows the chromatogram of acetone collected from the extract solution prepared at 350°C and 10 MPa. The collected acetone showed many peaks after the solvent peak. Acetic acid was not detected in the acetone but no further attempt was made to characterize the compounds. The effect of these compounds on the process with recycling of the solvent was not investigated.

4.7 Evaluation of Extracts in Plywood Adhesives

A potential use for the supercritical gas extraction products is as a partial substitute for phenol in phenol-formaldehyde (PF) adhesives for plywood manufacture. Mixes were prepared with 15% and 30% substitution of the phenol in the resin by extracts. The products evaluated were an acetone and a methanol extract obtained at 350°C and 10 MPa. Details of the preparation of the mixes and plywood samples are included as Appendix A.

To be acceptable as a plywood adhesive, the glue bond quality from both the dry and the wet (vapour-pressure) test must have an average wood failure of 80% or greater. Table 10 shows that substitution of 15 and 30% of each extract for

FIGURE 12

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
CHROMATOGRAM OF RECOVERED ACETONE

A. Technical grade acetone.

B. Acetone recovered during concentration of 350°C extract solution.

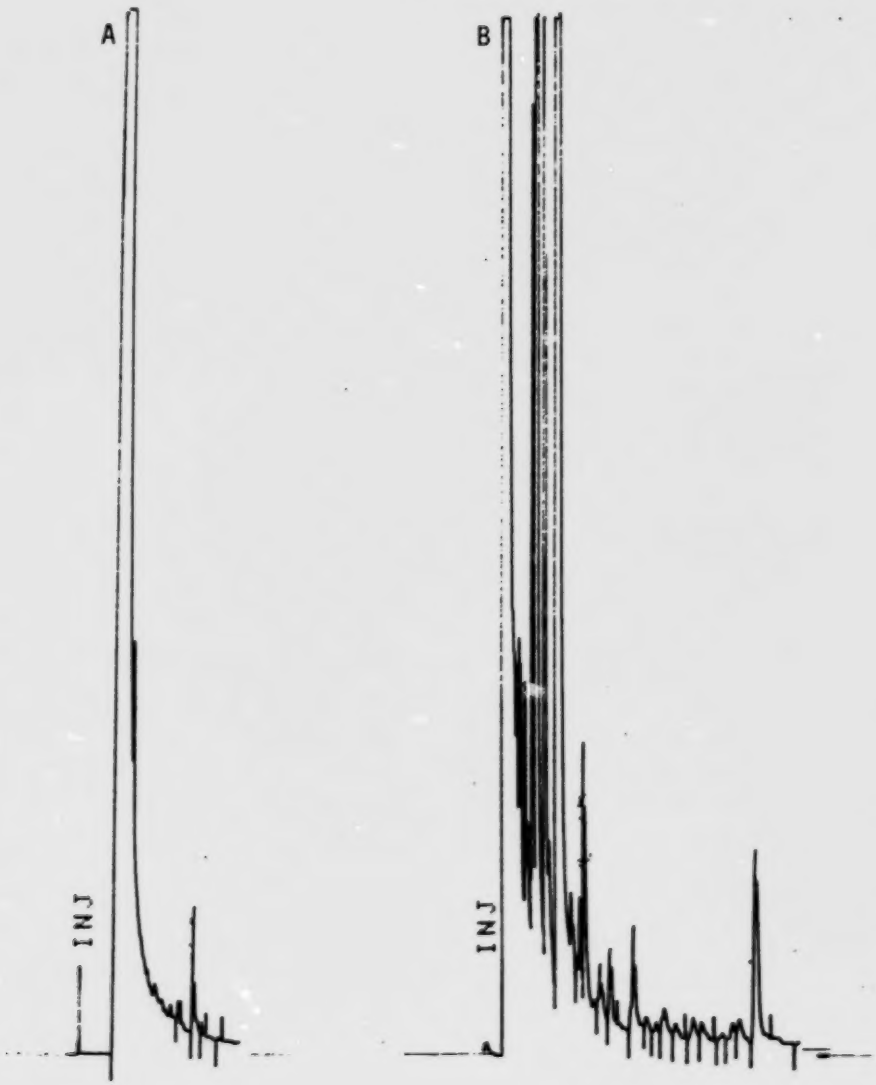


TABLE 10

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
EVALUATION OF ACETONE AND METHANOL
EXTRACTS IN PLYWOOD ADHESIVE MIXES

Description	Substitution of PF Resin %	Dry Test		Wet Test	
		Strength MPa	Wood Failure %	Strength MPa	Wood Failure %
Control	0	1.86	99	1.31	94
Methanol Extract 350°C, 10 MPa	15	1.59	97	1.24	61
	30	1.45	92	0.90	25
Acetone Extract 350°C, 10 MPa	15	1.72	92	1.24	24
	30	1.86	92	1.10	11
Acetone extract with:[a]					
5% paraformaldehyde	30	1.59	87	1.37	33
10% paraformaldehyde	30	1.93	100	1.17	47
15% paraformaldehyde	30	2.07	72	1.17	26
20% paraformaldehyde	30	1.86	73	1.10	26
Acetone extract reacted with formaldehyde solution before substitution.	30	2.07	92	1.45	44

[a] Paraformaldehyde added to mix before application to veneer, refer to Appendix A for details.

the PF resin gave wet test wood failures less than 80%. Addition of 10% paraformaldehyde to the acetone extract mix before application to the veneer increased the wet test wood failure from 11% to 47%. Reaction of the acetone extract with formaldehyde solution to form methylol groups increased the wood failure from 11% to 44%.

The dry test wood failure and bond strength were the same, with 30% substitution of the acetone extract, as those for the control samples. Therefore, the extract could be substituted at the 30% level for waferboard adhesives which do not require high wet test wood failure. However, this study was limited by both the time and amount of extract available. Further study of the extracts by a laboratory with more experience in the substitution of lignin derived materials in PF resin adhesives may result in the development of a mix with acceptable wet test wood failure.

4.8 Estimated Cost of Producing Crude Product in a Full Scale Plant

While yields of extract in excess of 70% can be obtained from wood using supercritical methanol and acetone, these yields are impractical at the moment in any large scale extraction plant for two main reasons. First, these high yields require that extractions be carried out at pressures as high as 28 MPa, which would require extraction vessels of such strength as to be uneconomical. Second, extract yields as high as 70% leave little residue for power generation. An extraction plant operating at this yield would not be self sufficient in the energy required to heat and compress the supercritical fluid. On the basis of such considerations, it has been estimated that a plant would only be in balance when the extract yield was 40% and the residue for power

generation amounted to 35% of the feedstock weight. Laboratory data have indicated that this is possible when the operating pressure and temperature are 10 MPa and 310°C, respectively, and the extraction solvent is acetone. These conditions are considered feasible for scale up from both an economic and technical standpoint.

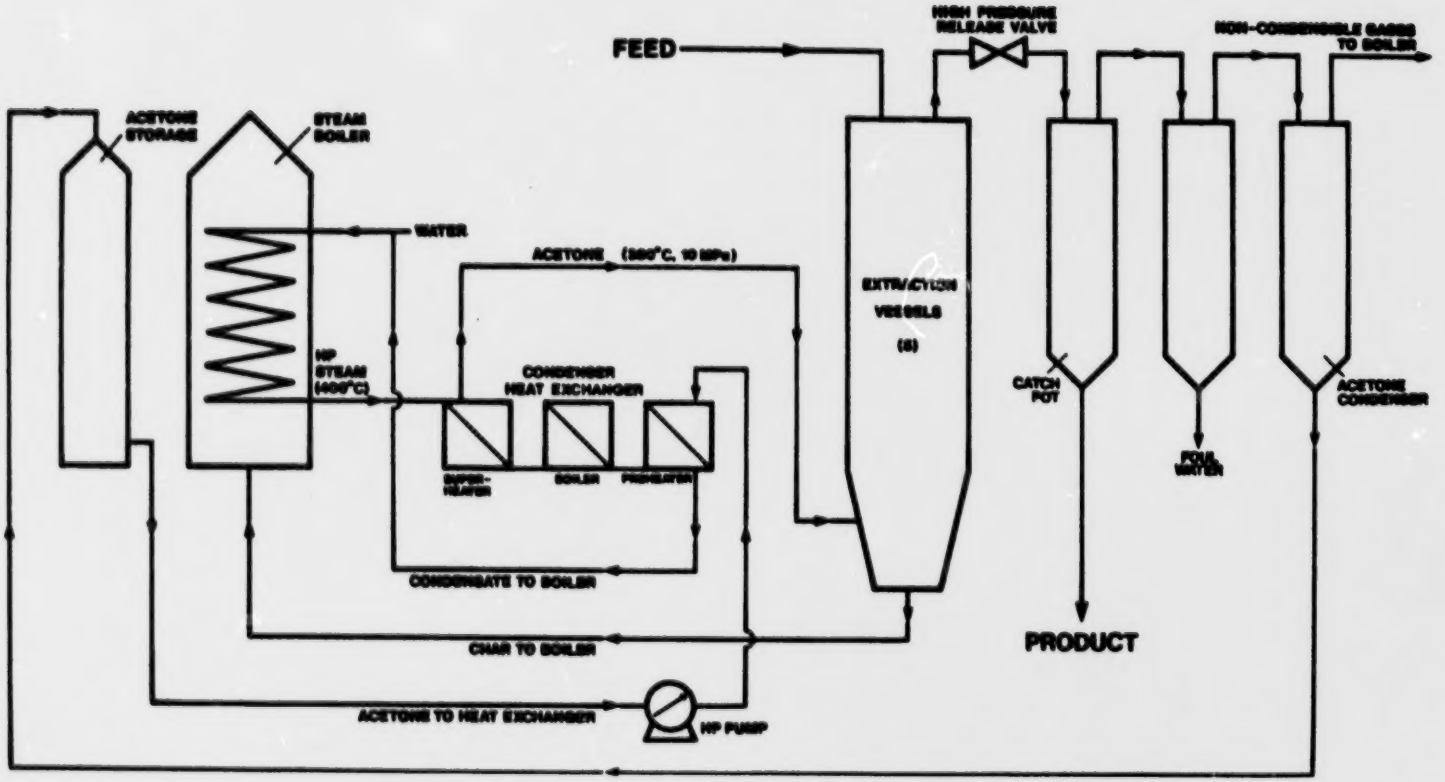
Figure 13 shows the proposed layout for an 800 barrel per day extraction plant. Five batch extractors, each with a capacity of 10 tonnes (ovendry basis), would be charged with wood and extracted with supercritical acetone generated from a pump and boiler. The cycle time would be 2.4 hours. This allows 10 cycles for each vessel and a total feedstock throughput of 500 tonnes per day. Following extraction, the solvent is removed from a catch pot, the foul water separated and condensed solvent recycled. On the basis of these assumptions and with current prices for a conventional boiler and heat exchanger, the total plant installation cost is estimated at $24.1 million. Over a 20 year write-off period, at 25% per year, this gives a capital depreciation cost of $25.1/barrel of product.

The solvent-to-feedstock weight ratio and loss of solvent, based on feedstock, were assumed to be 8:1 and 2%, respectively. Overhead costs, including solvent losses, are $16.9/barrel. Total production cost, including labour (13 men per shift), was $42/barrel, excluding land and feedstock costs. The detailed cost estimate is included in Appendix C.

In February 1981, an economic analysis was prepared of a plant using methanol at 350°C and 10 MPa to extract hog fuel (McDonald, 1981). A review of this analysis and attempts with our equipment to determine the actual solvent loss,

Figure 13

PROPOSED 800 BARREL/DAY PLANT FOR SUPERCRITICAL GAS EXTRACTION OF WOOD



rather than the assumed 0.5% loss based on similar work with coal, prompted a number of changes in the proposed plant with a consequent change in the product cost to $42 per barrel from $21 per barrel.

The changes made in the plant and cost estimate were:

1) The size of the plant was reduced to 800 barrels per day. The amount of product produced in the original plant (2,400 barrels per day), if the product were used as an adhesive substitute, would have beeen large compared to North American usage of phenol-formaldehyde resins for plywood manufacture. Phenol-formaldehyde resin usage in North America for 1979 was estimated to be 500 million pounds annually of dry PF solids (Sellers, 1981). An 800 barrel per day plant would have an annual output of about 130 million pounds which is still a large proportion of the annual PF usage. The reduction in size increased the cost per barrel because the economy of size was lost.

2) The solvent was changed from methanol to acetone because of the methanol loss through reaction with the product and residue, as shown by their increased methoxyl contents (refer to Section 4.5.2). An advantage in changing to acetone is that the latent heat of acetone, 521 joules/gram, is approximately half that of methanol.

3) The solvent temperature was lowered from 400°C to 350°C, because above 310°C no increase in yield was obtained with acetone at 10 MPa (Section 4.1).

4) The methanol boiler was replaced by a conventional steam boiler and a three stage countercurrent heat exchanger, for reasons of safety and availability.

5) The number of extraction vessels was increased from 2 to 5 to make the loading and unloading operations less critical for product flow.

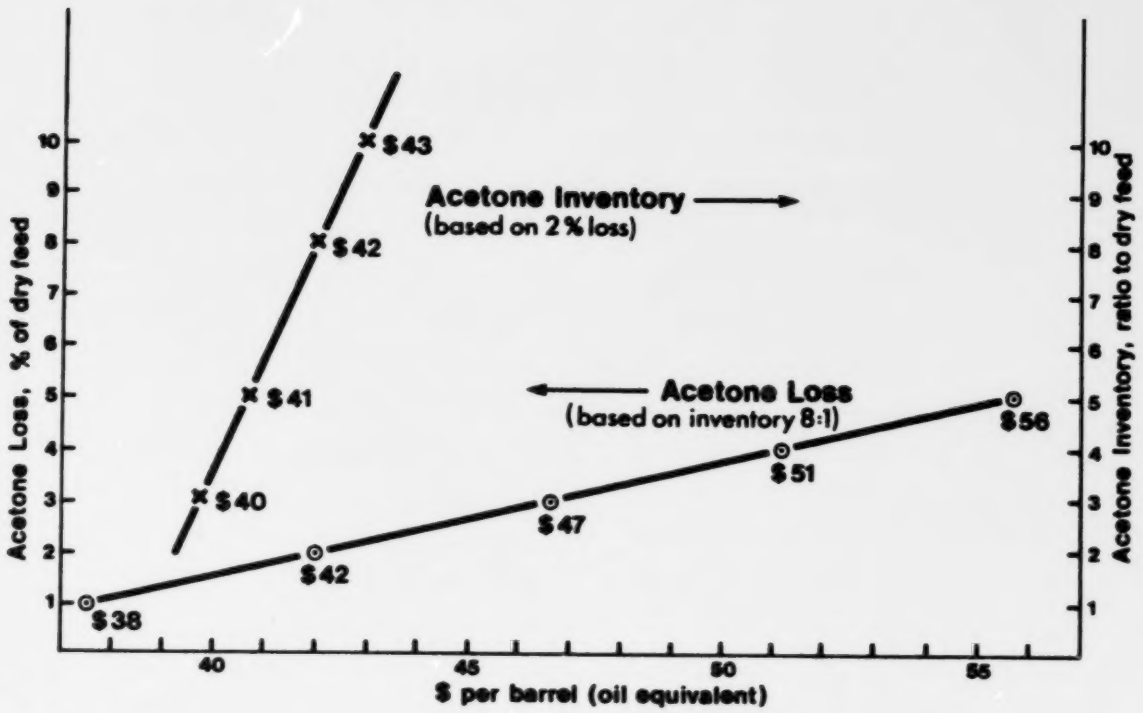
6) The acetone inventory was increased from 5:1 based on dry feed to 8:1. That is, for a reactor charge of 10 tonnes of dry feed (approximately 20-22 tonnes wet), 80 tonnes of acetone (at STP) would be pumped through the extraction vessels. The acetone inventory is based on one day's supply. The 8:1 ratio is close to laboratory experiment requirements, but is probably conservative on a larger scale. As shown in Figure 14, the cost per barrel is not very sensitive to changes in the ratio of acetone to dry feed.

7) The assumed acetone loss was increased from 0.5% of dry feed to 2%. That is, for a reactor charge of 10 tonnes of dry feed, 0.2 tonnes of acetone would be retained in the product, foul water and gas stream. Attempts with our equipment to determine the actual solvent loss were not successful. Our equipment held a dry feed charge of approximately 15 g. A 2% solvent loss would be 0.38 ml and our equipment was not sensitive enough to measure this small change in volume. Figure 14 shows that the cost per barrel is very sensitive to changes in the acetone loss. Therefore, the acetone loss is the prime area of concern in evaluating the proposed process.

Calculations of the effect of changes in the acetone inventory and acetone loss on the cost per barrel of extract are included in Appendix C.

Figure 14

SENSITIVITY OF EXTRACT COST TO ACETONE LOSS AND INVENTORY



5.0 RESULTS AND DISCUSSION: LOW TEMPERATURE EXTRACTIONS

The isolation of resin and fatty acids from Southern Pine and wax from Douglas-fir bark was studied. Supercritical fluids which are gaseous at ambient temperatures were used, carbon dioxide, nitrous oxide, propane and ethylene.

5.1 Extraction of Resin and Fatty Acids from Southern Pine

A preliminary investigation was carried out using carbon dioxide (T_c, 31°C; P_c, 7.9 MPa) to study the effect of equilibration time, temperature, pressure and particle size on the yield of resin acids from Southern Pine. A sample of chipped stump wood, supplied by Hercules Incorporated, from trees grown near Hattiesburg, Mississippi, was used throughout this study. The standard volume of gas passed through the wood was 85 litres measured at ambient temperature and pressure. The effect of increasing the gas volume was also studied. Sample size was 30 g of wet wood, equivalent to 19 g dry wood. All yield data are based upon weight of dry wood extracted. Product yields do not include turpentine, because of the drying technique.

5.1.1 Effect of Equilibration Time on Resin Acid Yields

The sample and gas were preheated for 30 minutes at the extraction temperature and pressure before starting the extraction. Table 11 shows that longer equilibration times did not increase the yield beyond 2.1%, whereas zero equilibration time reduced the yield to 1.6%. The composition of the extracts remained the same at equilibration times of 30, 60 and 90 minutes. Equilibrating

TABLE 11

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF SOUTHERN PINE:
EFFECT OF EQUILIBRATION TIME ON RESIN AND FATTY ACID YIELDS

Acid	Weight of Acid in Extract, mg				
	Soaking Time, mins. (40°C and 21 MPa)				
	zero	30	60	90	3 x 30 = 90
OLEIC/LINOLENIC	1.1	1.5[a] 1.7	1.6	1.7	1.9
LINOLEIC	2.3	2.9 3.6	3.0	3.3	3.4
PIMARIC	14.6	18.7 19.1	17.4	18.9	19.4
SANDARACOPIMARIC	6.6	7.9 8.0	7.5	8.5	7.9
ISOPIMARIC	28.6	34.5 35.6	32.5	35.9	34.4
LEVOPIMARIC/PALUSTRIC	78.4	98.4 104	94.7	104	95.8
DEHYDROABIETIC	15.6	19.5 19.3	18.4	19.2	20.6
ABIETIC	85.5	103 106	99.0	107	103
NEOABIETIC	37.6	44.3 50.0	51.5	58.8	43.1
TOTAL, mg	270	331 347	326	357	330
WEIGHT OF EXTRACT, mg	307	388	369	395	401
EXTRACT YIELD % DRY WOOD	1.6	2.1	2.0	2.1	2.0

[a] Samples analyzed two weeks apart.

the sample and gas for 30 minutes, passing 28 litres of gas through the sample and repeating the sequence twice, changed neither the resin acid yield nor the composition of the extract.

Stirring the sample and gas or shaking the extraction vessel may reduce the equilibration time to a few minutes without reducing the yield. Our equipment could not be adapted to try these techniques.

5.1.2 Effect of Temperature on Resin Acid Yields

Figure 15 shows that an increase in temperature from 35°C to 40°C did not change the yield. An increase from 40°C to 60°C decreased the yield from 2.1% to 1.4%. Table 12 shows that the composition of the extract changed as the temperature was increased above 40°C. The relative amounts of levopimaric, palustric and abietic acids in the extract decreased as the temperature increased.

The solvent power of supercritical fluids is usually greatest at a temperature just above the critical temperature. As the critical temperature of carbon dioxide is 31°C, it could be expected that the yield at 35°C would be greater than at 40°C. However, increasing the temperature increases the vapour pressure of the resin acids and between 35°C and 40°C the yield represents a compromise between these two effects (Williams, 1981).

5.1.3 Effect of Pressure on Resin Acid Yields

Figure 15 shows a large increase in yield from 0.1% to 2.1% as the pressure was increased from 10 to 21 MPa. As the pressure was increased from 21 to 62 MPa, the yield

Figure 15

SUPERCRITICAL CARBON DIOXIDE EXTRACTION: EFFECT OF TEMPERATURE AND PRESSURE ON RESIN ACID YIELD FROM SOUTHERN PINE

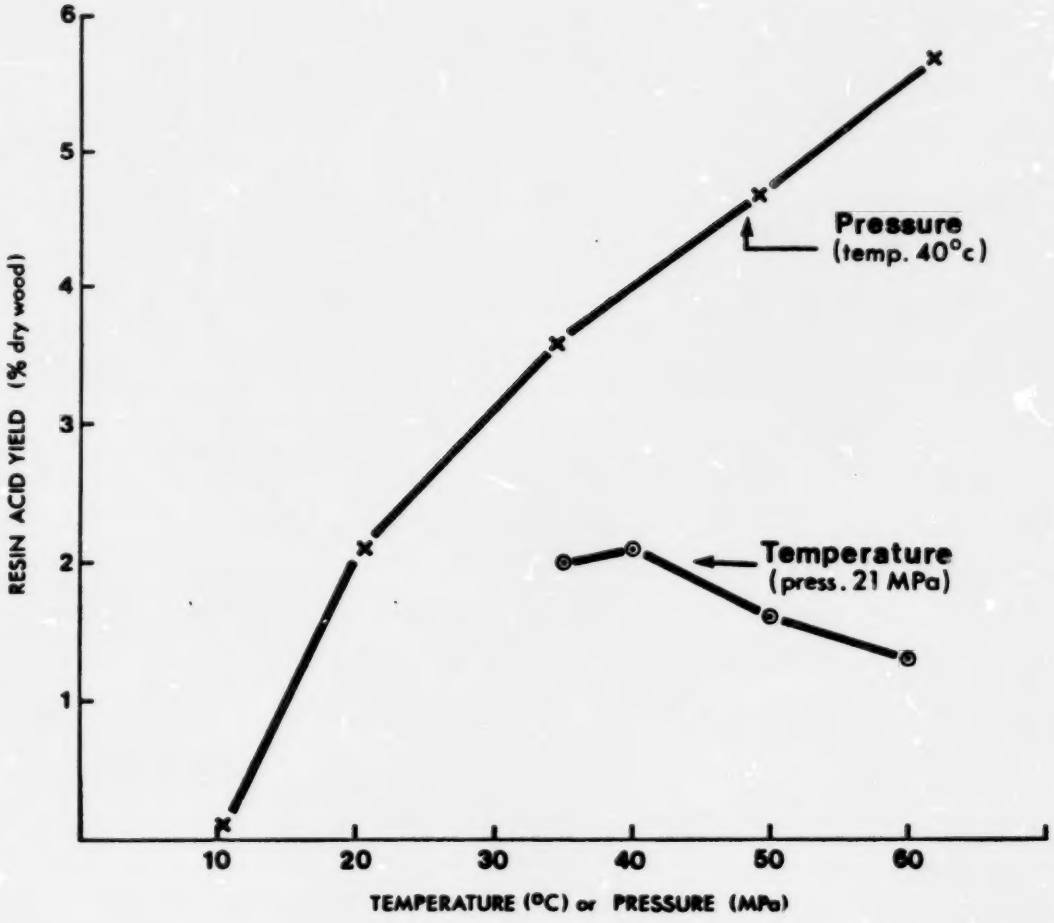


TABLE 12

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF SOUTHERN PINE: EFFECT OF TEMPERATURE ON RESIN AND FATTY ACID YIELDS[a]

Acid	Weight of Acid in Extract, mg			
	Extraction Temperature, °C			
	35	40	50	60
OLEIC/LINOLENIC	NOT ANALYZED	1.6	1.6	1.4
LINOLEIC		3.3	2.9	2.7
PIMARIC		18.9	16.6	14.0
SANDARACOPIMARIC		8.0	6.1	5.8
ISOPIMARIC		35.1	29.8	25.4
LEVOPIMARIC/PALUSTRIC		101	40.7	37.4
DEHYDROABIETIC		19.4	21.7	20.2
ABIETIC		104	62.5	55.6
NEOABIETIC		47.2	20.9	17.5
TOTAL, mg	-	339	203	180
WEIGHT OF EXTRACT, mg	380	388	317	269
EXTRACT YIELD % DRY WOOD	2.0	2.1	1.6	1.4

[a] Pressure, 21 MPa.

TABLE 13

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF SOUTHERN PINE: EFFECT OF PRESSURE ON RESIN AND FATTY ACID YIELDS[a]

Acid	Weight of Acid in Extract, mg				
	Extraction Pressure, MPa				
	10.3	20.7	34.5	48.3	62.1
OLEIC/LINOLENIC	trace	1.5[b] 1.6	2.6	2.8	3.1
LINOLEIC	trace	3.3 3.0	5.4	5.2	6.4
PIMARIC	0.3	16.3 17.4	38.1	46.0	52.7
SANDARACOPIMARIC	0.1	6.9 7.5	15.0	17.9	21.6
ISOPIMARIC	0.7	29.4 32.5	71.2	87.9	103
LEVOPIMARIC/PALUSTRIC	0.8	86.9 94.7	229	292	337
DEHYDROABIETIC	0.8	16.4 18.4	38.6	48.6	58.6
ABIETIC	0.8	88.1 99.0	249	325	380
NEOABIETIC	0.1	45.3 51.5	145	193	221
TOTAL, mg	3.6	294 326	794	1018	1183
WEIGHT OF EXTRACT, mg	20	415 369	690	909	1093
EXTRACT YIELD % DRY WOOD	0.1	2.1	3.6	4.7	5.6

[a] Temperature, 40°C.
[b] Duplicate experiments.

increased from 2.1% to 5.6%. The relative amounts of resin acids in the extracts, shown in Table 13, did not change significantly as the pressure was increased. Therefore, none of the resin acids were selectively extracted.

5.1.4 Effect of Particle Size on Resin Acid Yields

The Southern Pine wood was sieved to give three fractions; <2 mesh (32% by weight), 2-4 mesh (36%) and >4 mesh (32%). The smallest particle size gave the highest yield, 2.4%. The middle fraction gave a yield of 2.1% and the largest fraction 1.9%. The whole wood gave a yield of 2.1%.

These results indicate that the rate of diffusion of the fluid into the wood and the accessibility of the resin acids to the fluid have an effect on yield.

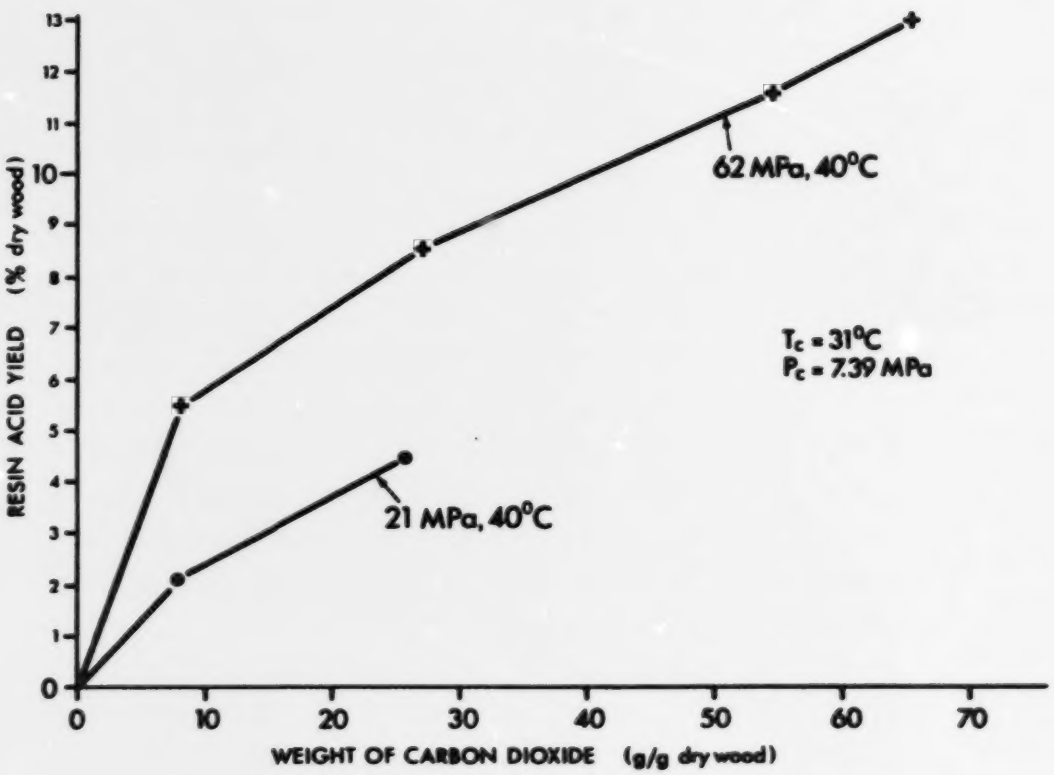
5.1.5 Relationship of Yield to Weight of Carbon Dioxide used in the Extraction

Figure 16 shows that increasing the amount of carbon dioxide used during the extraction, at a pressure of 62 MPa, increased the yield from 5.6% with 8 g CO_2/g dry wood to 13% with 66 g CO_2/g dry wood.

The amount of gas used was measured, in litres, at room temperature and pressure and converted to STP (0°C, 101.3 kPa). The relationship between yield and amount of gas depends on the sample size and moisture content of the sample. Therefore, the amount of gas was quoted as g CO_2/g dry wood to remove the variables of sample size, moisture content, room temperature and pressure.

Figure 16

SUPERCRITICAL GAS EXTRACTION OF RESIN ACIDS FROM SOUTHERN PINE: RELATIONSHIP OF YIELD TO WEIGHT OF CARBON DIOXIDE USED



The weight of resin acids extracted per 100 g of gas declined as the amount of carbon dioxide increased. Assuming 100 g of dry wood, 5.6 g of resin acids was extracted by 800 g of carbon dioxide, equivalent to 700 mg/100 g gas. To extract 13 g of resin acids would require 6,600 g gas, equivalent to 200 mg/100 g gas.

5.1.6 Resin Acid Yields with Nitrous Oxide, Ethylene, Carbon Dioxide and Propane

At 21 MPa, propane gave the highest yield of resin and fatty acids at 18.8%, followed by nitrous oxide 6.8%, ethylene 2.3%, and carbon dioxide which gave the lowest yield at 2.1% (Table 14). These yields were obtained after passing 5 to 8 g of gas per gram of dry wood through the sample.

The different molecular weights of the gases meant that extract yields could not be compared on the basis of volume of gas passed through the sample. Therefore, the volume of each gas, measured at room temperature and pressure, was calculated at STP (0°C, 101.3 KPa), converted to grams by dividing by 22.4 (one mole of an ideal gas at STP occupies 22.4 L) and multiplying by the molecular weight. The grams of gas was then divided by the grams of dry wood to give the weight of gas passed through the sample per gram of dry wood. About 30g of wet wood was used for each extraction, equivalent to about 19g of dry wood. Eighty-five litres of nitrous oxide, ethylene or carbon dioxide ($3ft^3$) was passed through the samples and the yield determined. Only 62 litres of propane was passed through the sample, because the valve blocked reducing the flow. This blockage was thought to be caused by the large amount of extract and by water condensing in the line between the extraction vessel and the pressure reducing valve. Better insulation of this line to maintain a temperature greater than 100°C should prevent blockage of the valve.

TABLE 14

SUPERCRITICAL GAS EXTRACTION OF SOUTHERN PINE:
RESIN ACID YIELDS USING PROPANE, NITROUS OXIDE,
ETHYLENE AND CARBON DIOXIDE

Pressure MPa	Yield % Dry Wood			
	Propane [a] (105°C) [d]	Nitrous oxide [b] (45°C)	Ethylene [c] (15°C)	Carbon dioxide [b] (40°C)
21 (3000 psig)	18.8	6.8	2.3	2.1
62 (9000 psig)	- [e]	14.2	6.9	5.6

[a] Propane extraction: 6 g gas/g dry wood, equivalent to 62 litres at room temperature and pressure.

[b] Nitrous oxide and carbon dioxide: 8 g gas/g dry wood, 85 litres at room temperature and pressure.

[c] Ethylene: 5.2 g gas/g dry wood, 85 litres at room temperature and pressure.

[d] Extraction temperature, approx. T_c + 9°C.

[e] Maximum pressure of pump, 34 MPa, prevented an extraction at 62 MPa.

Nitrous oxide gave the highest yield at 62 MPa of 14.2% (Table 14), ethylene gave 6.9% and carbon dioxide 5.6%. On the basis of the results at 21 MPa, propane would probably have given a greater yield than nitrous oxide.However, an extraction with propane could not be carried out at 62 MPa because the compressor required an inlet pressure of 4.8 MPa, while the propane cylinder had a pressure of only 0.89 MPa. Consequently, the propane extractions were carried out using the "high temperature" equipment with a limit of 34 MPa imposed by the Milton Roy pump.

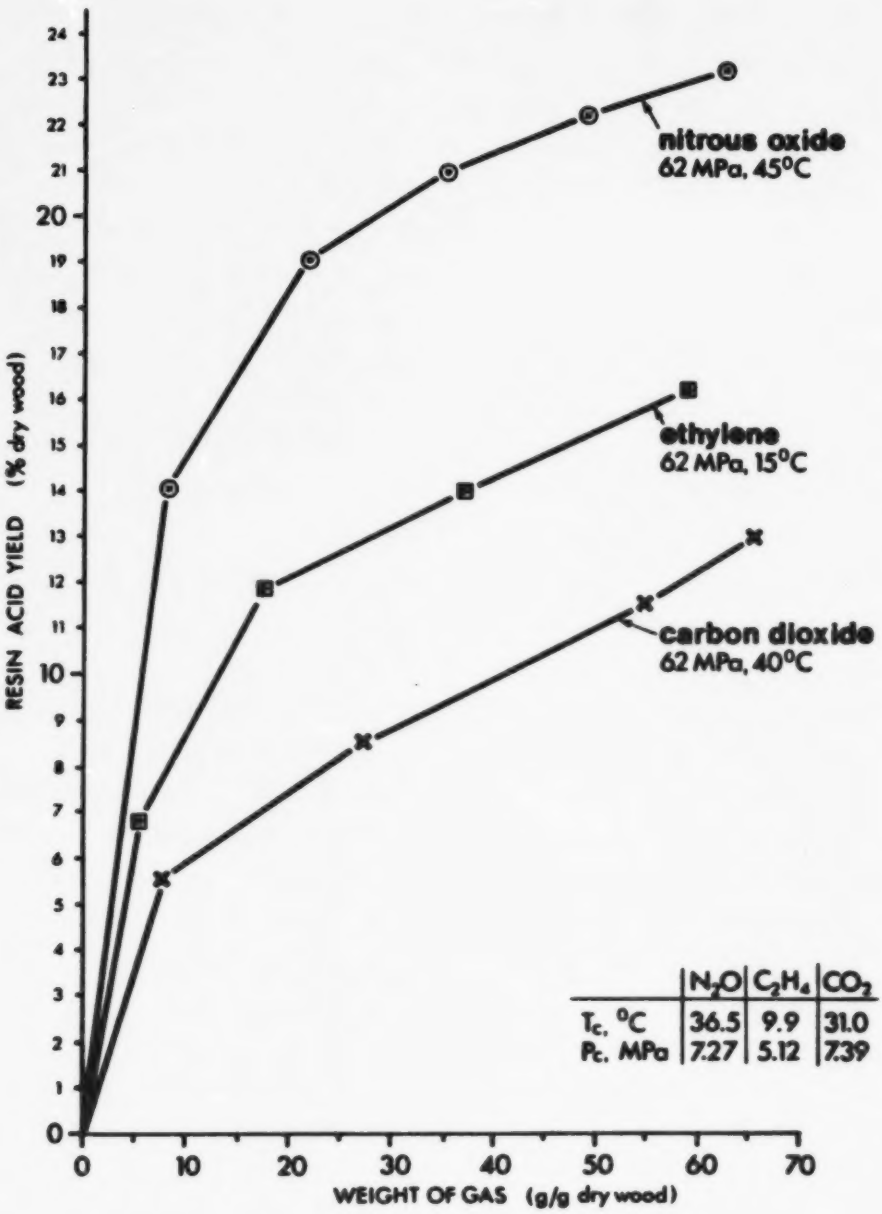
Table 14 shows also that tripling the extraction pressure from 21 MPa to 62 MPa gave an increase in yield with nitrous oxide of 2.1 times, 3 times with ethylene and 2.7 times with carbon dioxide. Therefore, increasing the pressure had less of an effect on the yield when a high yield had already been obtained at the lower pressure.

The effect of increasing the amount of gas passed through the sample on yield is shown in Figure 17 for nitrous oxide, ethylene and carbon dioxide at 62 MPa. For each gas, the yield increased as the amount of gas was increased. Nitrous oxide, for example, gave a yield of 14% with 8g of gas/g dry wood, increasing to 23% with 60g of gas/g dry wood.

The greater yields obtained with propane and nitrous oxide than with ethylene and carbon dioxide may be due to the fact that propane and nitrous oxide, unlike ethylene and carbon dioxide, have dipole moments and therefore can interact with polar groups in the resin and fatty acids. However, the dipole moment of propane is lower than that of nitrous oxide, 0.084D compared to 0.167D. The higher yield with propane than with nitrous oxide may be because the extraction

Figure 17

SUPERCRITICAL GAS EXTRACTION OF RESIN ACIDS FROM SOUTHERN PINE: YIELDS OBTAINED WITH NITROUS OXIDE, CARBON DIOXIDE AND ETHYLENE



temperature with propane, 105°C, was higher than with nitrous oxide, 45°C. This extraction temperature, necessary to exceed the critical temperature of propane (96.8°C), coupled with a greater vapour pressure of the resin acids at 105°C than at 45°C probably influenced the yield more than any other factor. The gas flow in the propane extractions was 5 ml/min., whereas the flow was about 6 L/min with nitrous oxide. The longer time that the propane was in contact with the wood may also have had some influence on the yield obtained.

The analysis of nitrous oxide, ethylene, carbon dioxide and propane extracts at 21 MPa for resin and fatty acids is given in Table 15. The analysis of the extracts obtained at 62 MPa is shown in Table 16. The composition of the extracts was similar, regardless of gas type and extraction pressure. For example, the nitrous oxide extract at 21 MPa contained the following acids: 32% abietic, 29% levopimaric and palustric, 13% neoabietic, 11% isopimaric, 6.3% dehydroabietic, 5.5% pimaric, 1.7% sandaracopimaric, 0.72% linoleic and 0.35% oleic and linolenic. The percentage of the extracts identified as fatty and resin acids was about 90%.

Table 17 shows the effect of increasing the amount of gas passed through the sample on the acids content of the extracts. Both the nitrous oxide and carbon dioxide extracts showed a decrease in the acids content of the extract as the amount of the gas was increased. For example, the nitrous oxide extract after passing through 150 g carbon dioxide was 90% acids, but the acid content dropped to 38% for the extract fraction collected between 400 and 660 g of gas.

TABLE 15

SUPERCRITICAL GAS EXTRACTION OF SOUTHERN PINE AT 21 MPa: ANALYSIS OF NITROUS OXIDE, ETHYLENE, CARBON DIOXIDE AND PROPANE EXTRACTS FOR RESIN AND FATTY ACIDS

Acid	Weight of Acid in Extract, mg			
	Nitrous Oxide 45°C	Ethylene 15°C	Carbon Dioxide 40°C	Propane 105°C
OLEIC/LINOLENIC	4.0	2.3	1.6	5.0
LINOLEIC	8.3	3.3	3.3	7.7
PIMARIC	63	22	19	147
SANDARACO-PIMARIC	20	7.0	8.0	43
ISOPIMARIC	125	42	35	302
LEVOPIMARIC/ PALUSTRIC	333	100	101	909
DEHYDROABIETIC	72	23	19	197
ABIETIC	371	112	104	1152
NEOABIETIC	154	60	47	500
TOTAL, mg	1150	371	339	3264
WEIGHT OF EXTRACT, mg	1250	420	388	3490
EXTRACT YIELD % DRY WOOD	6.8	2.3	2.1	18.6
% OF EXTRACT IDENTIFIED AS ACIDS	92	88	87	94

TABLE 16

SUPERCRITICAL GAS EXTRACTION OF SOUTHERN PINE AT 62 MPa:
ANALYSIS OF NITROUS OXIDE, ETHYLENE AND CARBON
DIOXIDE EXTRACTS FOR RESIN AND FATTY ACIDS

Acid	Weight of Acid in Extract, mg		
	Nitrous Oxide 45°C	Ethylene 15°C	Carbon Dioxide 40°C
OLEIC/LINOLENIC	3.7	3.8	3.1
LINOLEIC	5.7	4.9	6.4
PIMARIC	105	57	53
SANDARACO-PIMARIC	29	18	22
ISOPIMARIC	219	142	103
LEVOPIMARIC/ PALUSTRIC	684	334	337
DEHYDROABIETIC	128	68	59
ABIETIC	814	427	580
NEOABIETIC	379	214	221
TOTAL, mg	2368	1250	1183
WEIGHT OF EXTRACT, mg	2630	1270	1093
EXTRACT YIELD % DRY WOOD	14.2	6.9	5.6
% OF EXTRACT IDENTIFIED AS ACIDS	90	99	108

TABLE 17

SUPERCRITICAL GAS EXTRACTION OF SOUTHERN PINE:
EFFECT ON COMPOSITION OF NITROUS OXIDE AND CARBON DIOXIDE EXTRACTS
OF INCREASED WEIGHT OF GAS

Acid	Weight of Acid in Extract, mg			
	Nitrous oxide 62 MPa, 45°C		Carbon dioxide 62 MPa, 40°C	
	8 g gas/ g dry wood	35 g gas/ g dry wood[a]	8 g gas/ g dry wood	53 g gas/ g dry wood[b]
OLEIC/LINOLENIC	3.7	0.4	1.6	0.8
LINOLEIC	5.7	0.6	3.3	1.2
PIMARIC	105	17	19	25
SANDARACOPIMARIC	29	3.8	8	7.6
ISOPIMARIC	219	34	35	54
LEVOPIMARIC/ PALUSTRIC	684	104	101	152
DEHYDROABIETIC	128	23	19	31
ABIETIC	814	122	104	190
NEOABIETIC	379	54	47	87
TOTAL, mg	2368	357	339	549
WEIGHT OF EXTRACT, mg	2630	930	388	1180
EXTRACT YIELD % DRY WOOD	14.2 fraction: 2.0 total: 21.1		2.1 fraction: 3.0 total: 11.6	
% OF EXTRACT IDENTIFIED AS ACIDS	90	38	87	49

[a] Fraction collected from 21 to 35 g of gas/g dry wood.
[b] Fraction collected from 27 to 53 g of gas/g dry wood.

The chromatogram of a methylated nitrous oxide extract shown in Figure 18 is typical of those obtained. The peak at 10.50 is a neutral compound, present in both the non-methylated and methylated samples. The composition of resin and fatty acids in the extract was the same before and after saponification of the extract. Therefore, free acids were extracted from the wood.

Sitosterol, stigmasterol, juvabione, juvabiol and dehydrojuvabione were not present in a carbon dioxide extract examined for these compounds.

5.1.7 Comparison of Supercritical Gas Extraction with Solvent Extraction

Petroleum ether solvent extractions of Southern Pine gave resin acids yields of 12% after 6 hours and 18% after 40 hours, both extracts containing about 90% acids. The composition of the extracts was similar to that obtained with the supercritical fluids described in Section 5.1.6.

The amounts of resin acids extracted by petroleum ether are compared in Table 18 to the amounts extracted by propane, nitrous oxide, ethylene or carbon dioxide. Petroleum ether extracted 22 mg resin acids/100 g solvent in 6 hours, compared to propane which extracted 3250 mg/100 g in 3 hours. After a 15 minute extraction the amounts extracted at 21 MPa by nitrous oxide, ethylene and carbon dioxide were 860, 460, and 270 mg resin acids/100 mg gas, respectively. At 62 MPa, the amount of resin acids extracted was greater than at 21 MPa. For example, at 62 MPa nitrous oxide extracted 1770 mg resin acids/100g gas in 15 minutes. Therefore, the amounts of resin acids/100 g of extractant was greater using supercritical gases than petroleum ether.

FIGURE 18

SUPERCRITICAL GAS EXTRACTION OF RESIN ACIDS
FROM SOUTHERN PINE:
CHROMATOGRAM OF NITROUS OXIDE EXTRACT AT 62 MPa

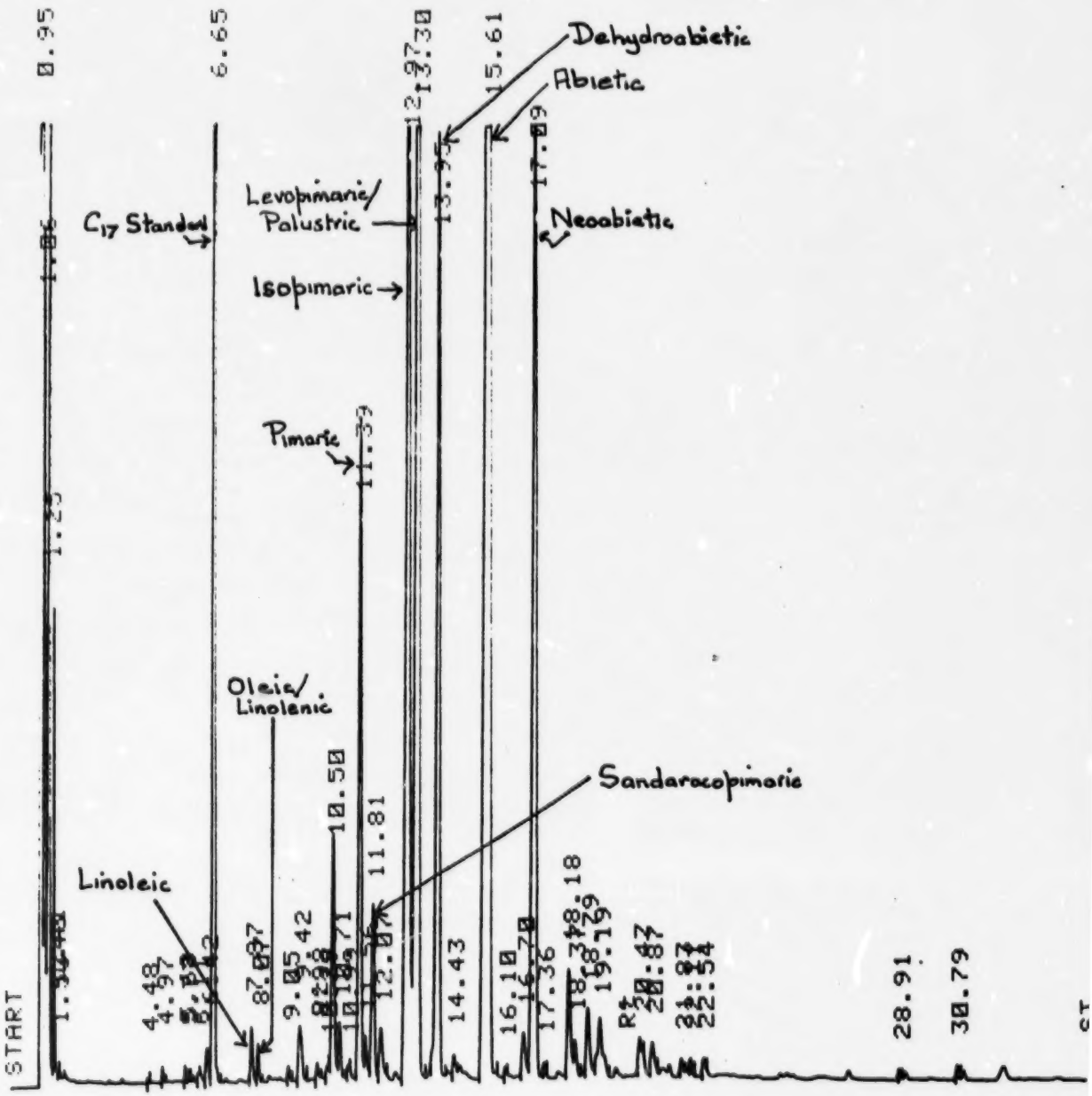


TABLE 18

SUPERCRITICAL GAS EXTRACTION OF SOUTHERN PINE:

AMOUNTS OF RESIN ACIDS EXTRACTED BY
PETROLEUM ETHER AND SUPERCRITICAL GASES

Extractant and Pressure	Time hr.	Sample Weight g (dry)	Weight of[a] Extractant g/g dry wood	Weight of Extractant g	Weight of Resin Acids Extracted mg	Amount Extracted mg Resin Acids/100g Extractant	Resin Acid Yield % dry wood
Petroleum ether[b]	6	2.5	552	1380	300	22	12
	40	3.7	2486	9200	670	7.3	18
Propane 21 MPa	3	19	6	110	3570	3250	19
Nitrous Oxide							
21 MPa	0.25	19	8	150	1290	860	6.8
62 MPa	0.25	19	8	150	2660	1770	14
62 MPa	2	19	60	1140	4370	380	23
Ethylene							
21 MPa	0.25	19	5	95	440	460	2.3
62 MPa	0.25	19	5	95	1290	1360	6.8
62 MPa	2	19	60	1140	3140	280	17
Carbon Dioxide							
21 MPa	0.25	19	8	150	400	270	2.1
62 MPa	0.25	19	8	150	1064	710	5.6
62 MPa	2	19	60	1140	2320	200	12

[a] Refer to Table 14 and Figure 17
[b] 6 cycles/hr; 40 g pet.ether/cycle.

Also, the extraction time was shorter. These results indicate that supercritical gas extraction has potential as a replacement of solvent extraction for the isolation of chemicals from forest products. Petroleum-based solvents are more expensive than these gases and an energy intensive distillation is required to separate the products.

The yield obtained by petroleum ether was enhanced by solvent extraction of the residue from the supercritical carbon dioxide extraction. At 62 MPa and using 8 g CO_2/g dry wood a yield of 5.6% was obtained. Petroleum ether extraction of the residue for 6 hours gave a further 19.1% yield for a total of 24.7%, with a resin acid content of over 90%. Petroleum ether extraction of the original wood for 6 hours gave a yield of 11.5%; after 40 hours 18.1%. The yield from the residue by petroleum ether extraction suggests that the carbon dioxide extraction, possibly as a result of the pressure applied to the wood, makes the resin acids more accessible to the solvent.

5.1.8 Effect of Source and Species of Pine on Resin Acid Yield

The source of the Southern Pine and the species of Pine had a marked effect on the yield and acids content of carbon dioxide extracts. Two samples of Southern Pine supplied by Hercules Incorporated were tested. One sample was chipped wood from old stumps collected at Hattiesburg, Mississippi. This sample called "Hattiesburg" was used for all the runs described in previous sections. The other sample, "Stumpwood", was a mixed sample of chipped fresh slash pine stumpwood from two sites in Lamar County, Mississippi; a 26 year old tree near Derby and an 18 year old tree near Lumberton. The samples were stored in a freezer until tested.

One sample of Lodgepole pine, "Lodgepole", the local British Columbia species was tested. The sample was collected from McCulloch Custom Log House Limited, Brittania Beach, and stored in a freezer.

At 21 MPa and using 8 g CO_2/g dry wood the yields were 2.1% from "Hattiesburg" and 1.1% from both "Stumpwood" and "Lodgepole". The resin acids content of the extracts was about 90% for "Hattiesburg", 55% for "Stumpwood" and 35% for "Lodgepole".

The "Stumpwood" sample was expected to give results similar to those obtained with the "Hattiesburg" sample. Abietic acid was not detected in the "Stumpwood" sample althougn this acid was the most abundant in the "Hattiesburg" sample. Deterioration of the "Stumpwood" sample may have occurred with abietic acid undergoing disproportionation reactions.

Solvent extractions of the three samples for 40 hours with petroleum ether gave yields of 18% for "Hattiesburg", 3.5% for "Stumpwood" and 4.4% for "Lodgepole". Similar to the carbon dioxide extracts, the acids content of the three petroleum ether extracts were about 90%, 65% and 40% respectively.

5.1.9 Extraction of Turpentine from Southern Pine

The major terpene found was α-pinene, along with β-pinene, p-cymene and β-phellandrene. Quantitative analysis was carried out for α- and β-pinene in two carbon dioxide extracts. At 21 MPa the yield of α-pinene was 0.85% based on dry wood and β-pinene, 0.18%. At 62 MPa, 1.0% α-pinene and 0.22% β-pinene was extracted. Turpentine yields are not included in the extract yields quoted

previously, because the terpenes were evaporated while drying an aliquot of the sample to determine the yield. The turpentine results are based on a 30 g sample of wet wood (19 g dry) using 150 g of carbon dioxide (8 g CO_2/g dry wood) for the extraction.

Figure 19 shows the numerous peaks obtained in the turpentine analysis, only a few of which were identified.

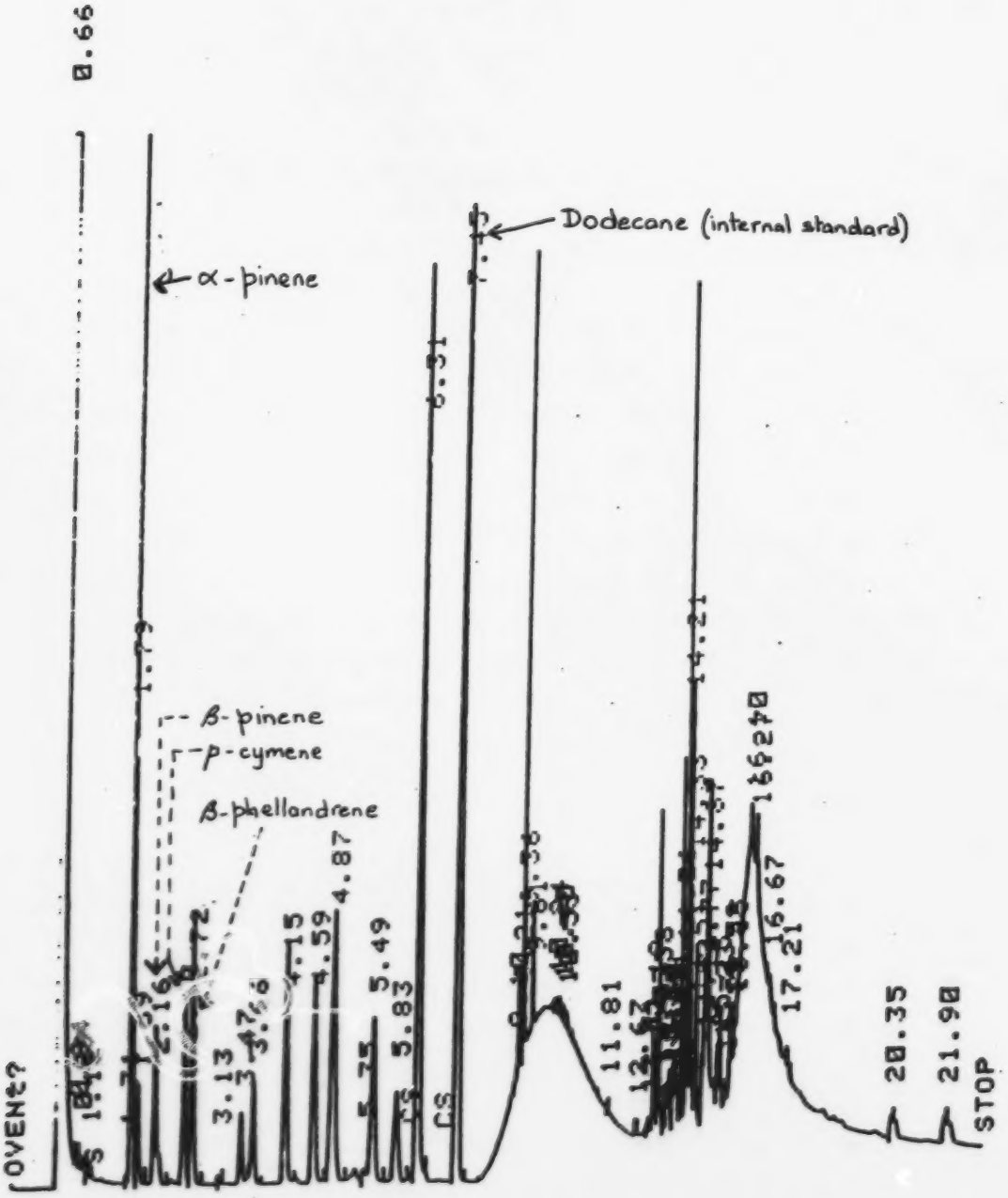
5.2 Extraction of Wax from Douglas-fir Bark

The relationships of equilibration time, temperature and pressure to product yield established for resin acids extraction were assumed to apply to wax extraction. The experiments described in this section were carried out with dried and sized samples of Douglas-fir bark obtained from Weyerhaeuser Limited; Silvacon 383 and Silvacon 387 Mill B bark, Test 1 (MBB). Silvacon 383, the coarser of the samples was mainly >28 mesh (59%). Silvacon 387, the finer sample was mainly <200 mesh (40%). The wax content of both Silvacons was given as 10%, obtained by initial extraction with an aliphatic hydrocarbon solvent and subsequently with an aromatic hydrocarbon solvent or a halogenated aliphatic hydrocarbon (Trocino, 1974). The first solvent extraction was stated to give a light yellow to light brown wax; the second extraction a brown to red brown wax. All the supercritical gas extracts and petroleum ether solvent extracts were a pale yellow.

The equilibration time for the supercritical gas extractions was 30 minutes, and the extraction temperature about 9°C above the critical temperature of the gas. Sample size was 40 g, equivalent to 36.7 g dry bark. All wax yields are the weight of extract expressed as a percentage of dry bark in the sample.

FIGURE 19

SUPERCRITICAL CARBON DIOXIDE EXTRACTION
OF SOUTHERN PINE:
CHROMATOGRAM OF TURPENTINE AT 62 MPa



5.2.1 Wax yields using Propane, Nitrous Oxide, Carbon Dioxide and Ethylene

Table 19 shows that at 21 MPa propane gave the highest yield, 5.5%. At 62 MPa, nitrous oxide gave the highest yield, 2.7%. A propane extraction was not carried out at 62 MPa because the maximum pump pressure was 34 MPa.

Extraction of resin acids from Southern Pine with propane also gave a high yield, nitrous oxide giving the next highest yield. The wax yields obtained using carbon dioxide were higher than those with ethylene, whereas the reverse was found in the resin acid extractions. The discussion in Section 5.1.6 of the effect of the dipole moment of the gas on resin acid yields, and the effects of the higher extraction temperature and lower flow rate of propane is relevant to these results.

Figure 20 shows the effect on wax yields of increasing the amount of gas passed through the samples. For example, the yield using nitrous oxide increased from 2.4% with 154 g of gas to 3.7% with 1140 g of gas (31 g N_2O/g dry wood). These results were obtained using Silvacon 387.

Table 20 shows that the wax yields using nitrous oxide were higher from Silvacon 383 than those from Silvacon 387. Carbon dioxide gave the reverse, with Silvacon 383 wax yields lower than those from Silvacon 387.

TABLE 19
SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:
WAX YIELDS WITH PROPANE, NITROUS OXIDE, CARBON
DIOXIDE AND ETHYLENE

	Wax Yields, % Dry Bark [a]			
Pressure MPa	Propane [b] 105°C	Nitrous oxide [b] 45°C	Carbon dioxide [b] 40°C	Ethylene [c] 15°C
21 (3000 psig)	5.5	2.2	1.1	0.54
62 (9000 psig)	-[d]	2.7	1.8	0.82

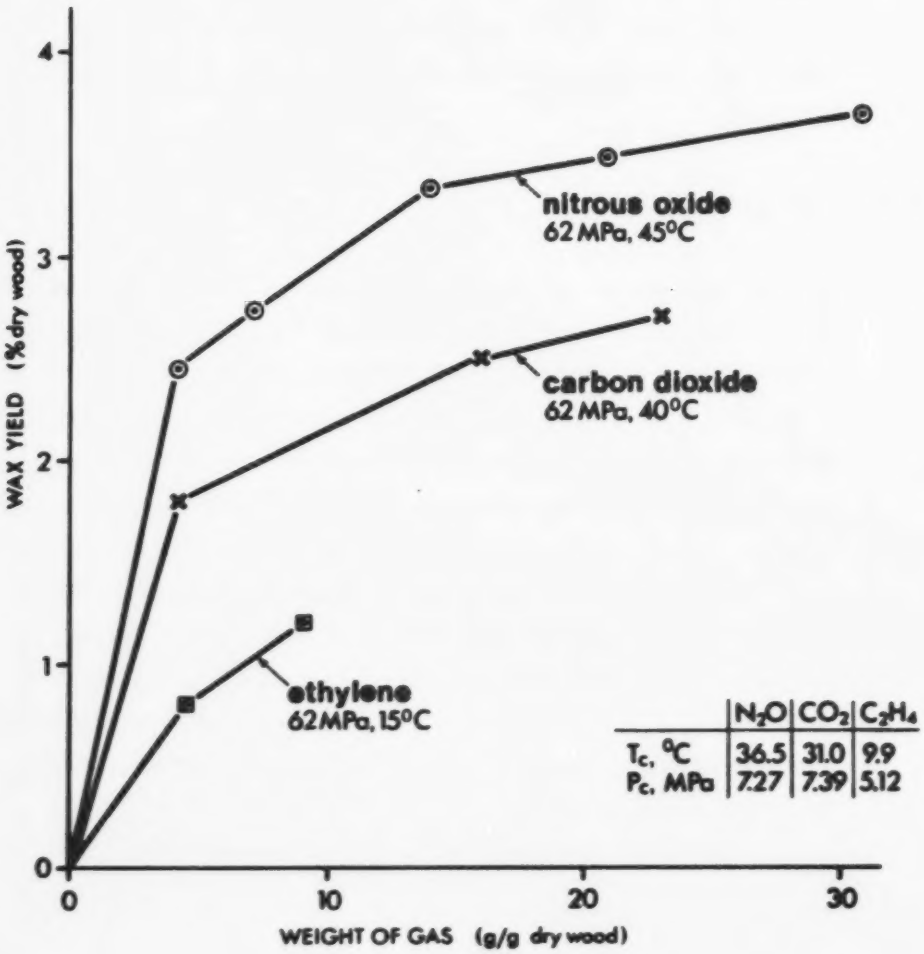
[a] Silvacon 387, Mill B bark, test 1.
[b] 4.2 g of gas/g dry bark ie., 153 g of gas.
[c] 4.4 g of gas/g dry bark ie., 162 g of gas.
[d] Maximum pressure of pump, 34 MPa, did not permit a run at 62 MPa.

TABLE 20
SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:
WAX YIELDS FROM SILVACON 383 AND SILVACON 387

Description	Gas	Yield % of Dry Bark	Pressure MPa
Silvacon 383	Carbon dioxide	0.5	21
		0.8	62
	Nitrous oxide	2.6	21
		3.3	62
Silvacon 387	Carbon dioxide	1.1	21
		1.5	62
	Nitrous oxide	2.2	21
		2.7	62

Figure 20

SUPERCRITICAL GAS EXTRACTION OF WAX FROM DOUGLAS-FIR BARK YIELDS OBTAINED WITH NITROUS OXIDE, CARBON DIOXIDE AND ETHYLENE



5.2.2 Comparison with Solvent Extractions

Iso-octane solvent extraction of Silvacon 387 for 6 hours gave a wax yield of 8% compared to petroleum ether yields of 1.5% after 6 hours and 2.3% after 40 hours. The petroleum ether extract had the same pale yellow colour as the supercritical gas extracts, whereas the iso-octane extract was brown. The yield with petroleum ether after 6 hours was similar to the carbon dioxide yield of 1.1% obtained in 15 minutes using 153 g of gas. The amount of wax extracted at 21 MPa using 153 g of propane, nitrous oxide and carbon dioxide was 1300, 530 and 260 mg wax/100 g gas, respectively. Petroleum ether extraction of 8.5 g dry bark for 6 hours using 230 g solvent/hour with a yield of 1.28 g wax, gave an extracted amount equal to of 9 mg wax/100 g solvent.

5.2.3 Analysis of Waxes

Gas chromatograms of wax extracts are shown in Figures 21 to 24. The nitrous oxide extract at 21 MPa (Figure 21) was similar to the nitrous oxide extract at 62 MPa (Figure 22), with five major peaks between 16 and 30 minutes. The carbon dioxide extract (Figure 23) showed the same five major peaks as the nitrous oxide extracts and a few additional minor peaks. The propane extract (Figure 24) showed four of the main peaks in the nitrous oxide extract plus two large peaks present only as minor components of the nitrous oxide extract. The small peak at 39.21 has been tentatively identified as β-sitosterol. The first major peak in each chromatogram, at about 5 minutes, was an internal standard, heptadecanoic acid.

FIGURE 21

SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:
CHROMATOGRAM OF NITROUS OXIDE EXTRACT AT 21 MPa

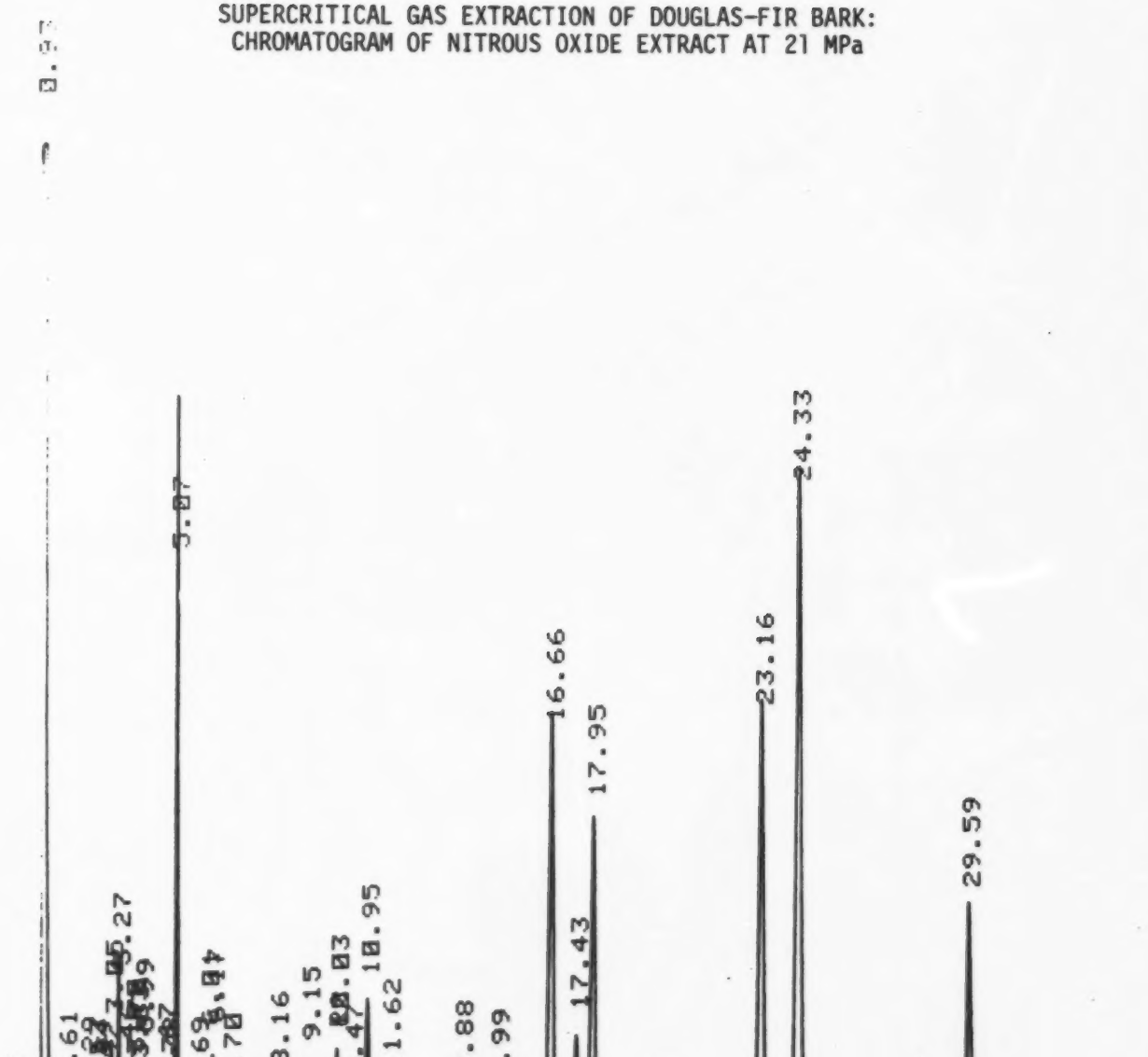


FIGURE 22

SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:
CHROMATOGRAM OF NITROUS OXIDE EXTRACT AT 62 MPa

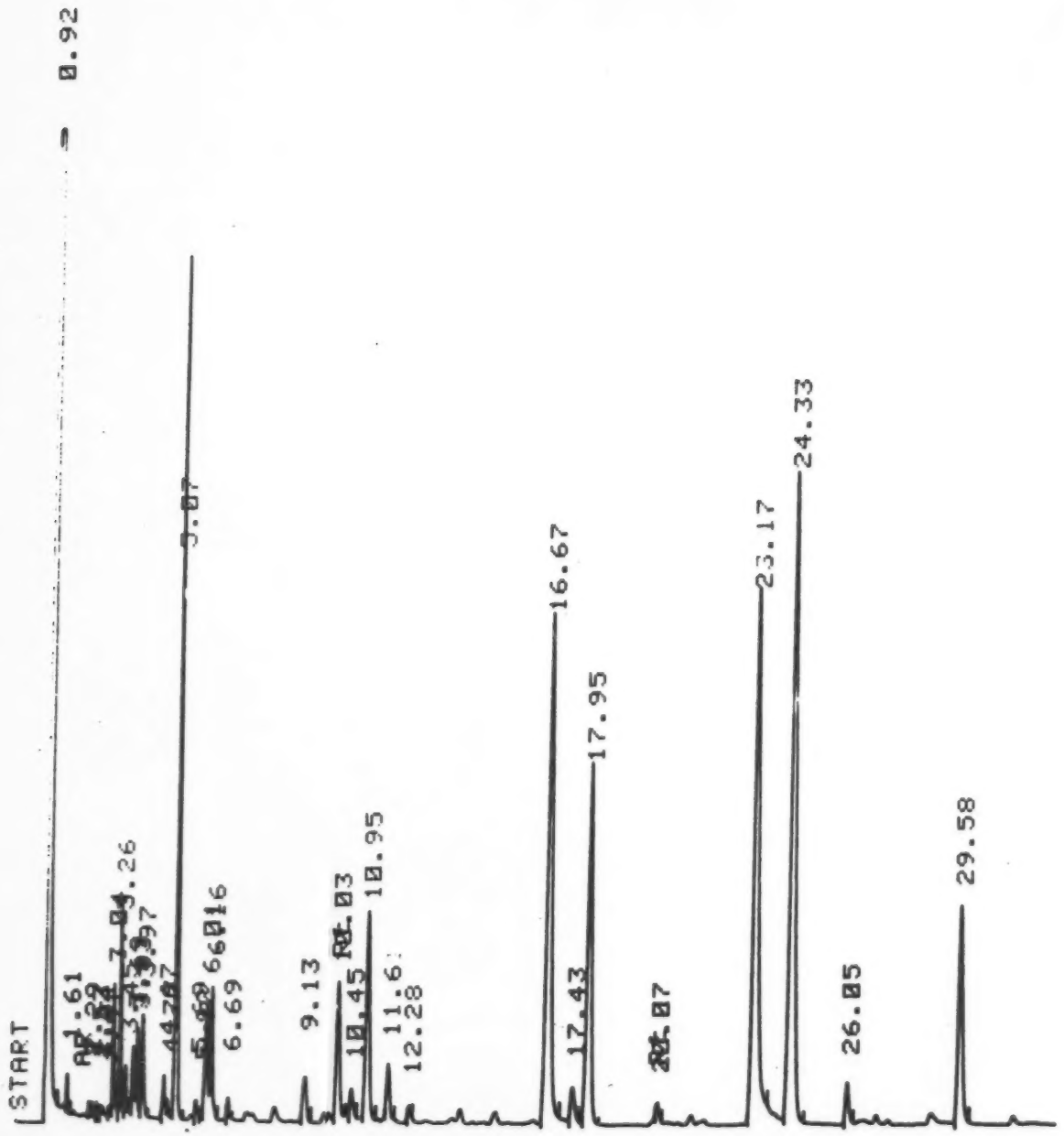


FIGURE 23

SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:
CHROMATOGRAM OF CARBON DIOXIDE EXTRACT AT 21 MPa

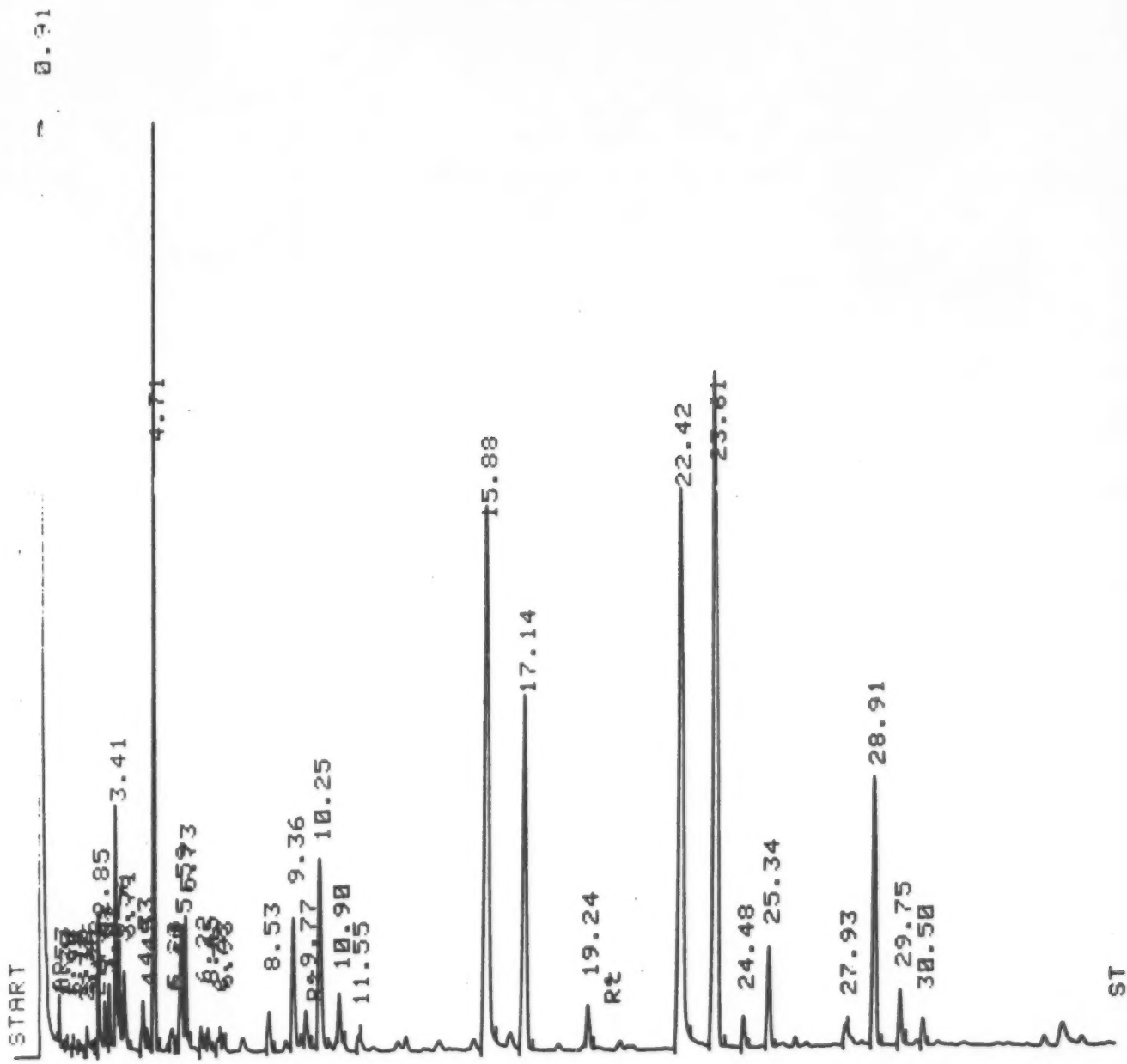
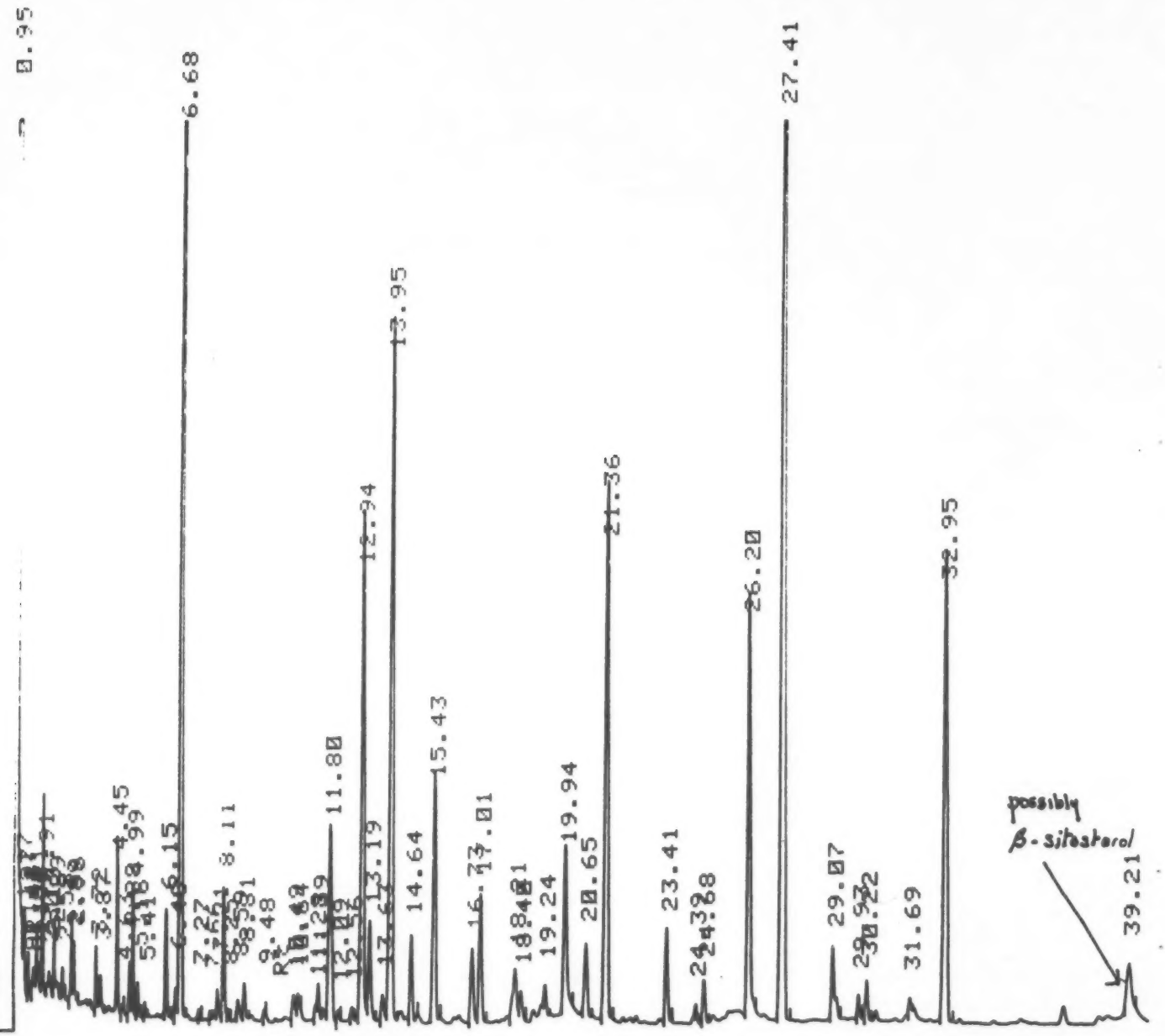


FIGURE 24

SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:
CHROMATOGRAM OF PROPANE EXTRACT AT 21 MPa



Gas chromatography and mass spectrometry of the nitrous oxide extract (Figure 21) did not give positive identification of the major peaks. Four compounds were tentatively identified as 1-octadecanol (C_{18}, stearyl alcohol), triacontanoic acid (C_{30}, melissic acid), 2-methyl, 1-hexadecanol (C_{17} alcohol) and tetracosanoic acid (C_{24}, lignoceric acid).

The main components identified in the solvent extracted commercial wax were stated to be lignoceric acid (19.7%); behenic acid, C_{22} (7.4%); cerotic acid, C_{26} (5.6%); behenyl alcohol, C_{22} (9.9%); and lignoceryl alcohol, C_{24} (8.7%) (Trocino, 1974). The tentative identification of the components in the supercritical nitrous oxide extract does not agree with that for the components in the commercial wax.

The saponification number, melting point range and elemental analysis of a few wax extracts are given in Table 21. The saponification number of the four supercritical gas extracts ranges from 100 to 130 mg KOH/g, the differences not being considered significant. By comparison, Carnuba wax has a saponification number of 72-85 mg KOH/g, indicating that the supercritical gas extracts contain more esterified acids than Carnuba wax.

The waxes melted over a fairly wide range of temperature. The nitrous oxide extracts had the largest range, 35 to 75°C. Carnuba wax has a higher melting point over a narrow range, 83 to 86°C.

TABLE 21

SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:[a] SAPONIFICATION NUMBER, MELTING POINT RANGE AND ELEMENTAL ANALYSIS OF WAXES

Description	Saponification Number	Melting Point Range	Elemental Analysis			
	mg KOH/g	°C	%C	%H	%N	%O[b]
Nitrous oxide						
21 MPa	120	35 - 75	74.86	11.42	0.04	13.68
62 MPa	120	36 - 74	74.71	11.21	0.04	14.04
Carbon dioxide						
21 MPa	-	-	77.37	11.64	0.04	10.95
62 MPa	110	30 - 45	76.55	10.98	0.04	12.43
Ethylene						
21 MPa	100	<30	-	-	-	-
62 MPa	130	30 - 45	-	-	-	-
Propane	115	45 - 55	-	-	-	-
Petroleum ether solvent extraction	-	-	77.14	11.42	0.05	11.39

[a] Silvacon 387, MBB
[b] Calculated by difference.

The carbon dioxide extracts had slightly higher carbon contents, 77%, than the nitrous oxide extracts, 75%. The petroleum ether solvent extract had a similar elemental analysis to the carbon dioxide extracts. A table summarizing the elemental analysis of wax extracts obtained by supercritical gas extraction and by solvent extraction is included in Appendix D.

5.3 Extraction of Hemlock

Hemlock wood was extracted with nitrous oxide and carbon dioxide at 62 MPa. Extract yields were 0.14% and 0.08%, respectively. The extracts were examined by thin layer chromatography for the presence of conidendrin but none was detected.

6.0 CONCLUSION

Liquefaction of wood was achieved by supercritical gas extraction using organic solvents. Yields of liquid products in excess of 70% based on dry wood, were obtained with acetone and methanol at 360°C and 28 MPa (4,000 psig). Acid pretreatment of wood gave yields in excess of 70% at a lower temperature (260°C) and pressure (10 MPa).

Analysis of liquid products obtained from Western red cedar has identified levoglucosan and substituted guaiacols.

Up to 30% of phenol in phenolic resins was replaced by supercritical gas extracts, with glue bond quality acceptable for waferboard applications but not for plywood.

An economic analysis, based on laboratory data and current engineering technology, gave a product cost of $42 per barrel for an 800 barrel per day plant, excluding land and feed costs. Acetone was the preferred solvent because methanol was shown to react with the feed. Extraction conditions of 330°C and 10 MPa were chosen to give a product yield of 40%, leaving a residue of 35% to provide fuel for the boiler.

The chemical composition of the liquid products obtained by supercritical gas extraction of wood indicated that they were not upgraded significantly compared with the feed. These products would not be directly marketable as liquid fuels but would require upgrading to produce marketable commodities. The low phenolic content of the extracts indicates that further processing would be required to produce a feedstock for the production of chemicals.

Chemicals were selectively extracted from wood and bark, employing supercritical fluids which are gaseous at room temperature. Propane, nitrous oxide, carbon dioxide and ethylene extracted resin acids from Southern Pine and wax from Douglas-fir bark. Propane gave the highest yields of resin acids and wax at 21 MPa (3,000 psig). Resin acids yield was 18.8% and wax yield 5.5%. About five grams of propane per gram of dry wood was required to obtain t ese yields. Using conditions similar to those of the propane extraction, nitrous oxide gave a resin acids yield of 6.8%, ethylene gave 2.3% and the lowest yield, 2.1%, was obtained with carbon dioxide.

Yields of wax at 21 MPa, by comparison with that using propane, were 2.2% using nitrous oxide, 1.1% using carbon dioxide and 0.5% with ethylene.

Higher yields of resin acids and wax were obtained by increasing the extraction pressure to 62 MPa (9,000 psig). Increasing the amount of gas passed through the sample also increased the yields.

The amount of resin acids extracted per gram of gas was greater with all four supercritical fluids than the amount extracted per gram of petroleum ether by solvent extraction. As well, the extraction time was shorter for supercritical gas extractions than for solvent extraction. Separation of the product from the supercritical gas was readily achieved by reducing the pressure.

Chemicals isolated by supercritical gas extraction would be directly marketable. This technique would reduce the use of petroleum-based solvents for the isolation of chemicals from forest products and eliminate the energy intensive distillation required to separate the solvent from the product.

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APPENDIX A

PREPARATION AND EVALUATION OF PLYWOOD ADHESIVES

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PREPARATION AND EVALUATION OF PLYWOOD ADHESIVES

The procedures and materials used to prepare adhesive mixes and plywood samples were provided by Forintek Canada Corp., Western Laboratory.

Borden Chemical's phenolic resin PF 659 was used in adhesive mixes, based on the standard plywood adhesive mix shown in Table A-1. A limited amount of supercritical gas extracts was available for testing, so a batch size of 80g total was used in this study. Control samples were prepared with batch sizes of 80g and 855g, one quarter of the standard recipe. As shown in Table A-2, the smaller batch size did not change the glue bond quality of the control. To increase the viscosity of the 80g batches, corn cob filler was reduced by 25% and the wheat flour increased as shown in Table A-1. The solids content and resin content (or resin plus extract) of the mixes were maintained at the levels in the standard mix.

The first portions of resin and water were mixed with the corn cob filler for 3 minutes, using an electric stirrer. The wheat flour and soda ash were added and the mixture stirred for 20 minutes. The second portions of resin and water were added and the mixture stirred for a few minutes. To increase the viscosity of the mixture, the mix was allowed to stand for as long as possible, but not overnight.

Douglas-fir veneer 38cm X 38cm was used to prepare plywood samples. The veneer was dry and was stored in a warm dry room. The adhesive was applied at the rate of 0.032 g/cm^2 (66 $lbs/1000\ ft^2$) to the veneer with the aid of a comb. Three sheets of veneer were weighed, adhesive applied to both sides of the centre sheet and the sheets reweighed to determine the actual amount of adhesive applied.

After 10 minutes the sheets were pressed in an Elm Engineering Works press with a 10" diameter shaft at a pressure of 1.6 MPa (230 psi) and temperature of 200°C for 6 minutes. The glueline temperature was 150°C for at least 2 minutes and was measured by inserting a thermocouple between the sheets during preparation of the sample. The pressed samples were hot stacked under a weight and cooled overnight.

Shear test specimens were prepared according to the requirement of the Canadian Standards Association for testing Douglas-fir plywood, CSA Standard 0121-M1978. The glue bond quality was determined by testing half the specimens dry and the other half wet after being conditioned in the Vacuum Pressure cycle. The bond strength was measured in psi by tension loading to failure in a shear testing machine. After testing, the percentage of wood failure was determined visually. The glue bond quality was acceptable if the average wood failure of all specimens was 80% or greater and the dry strength was 1.7 to 2.1 MPa.

Paraformaldehyde was added to mixes prepared with the acetone extract. The weight of paraformaldehyde added was 5%, 10%, 15% or 20% of the weight of extract and was added to the mix before spreading the adhesive on the veneer. Table A-1 shows the ingredients in the mix with 30% substitution of extract and 10% addition of paraformaldehyde.

Formaldehyde solution, 47% by weight, was added to the acetone extract and allowed to react in a closed container for 21 hours at 45°C. Formaldehyde was added equivalent to 15% of the weight of extract. The free formaldehyde was determined by titration with sodium sulphite initially and after 2, 4 and 21 hours. After 4 hours, no free formaldehyde was detected. A further 10% formaldehyde by weight of extract was added and free formaldehyde was detected after 21 hours. The amount of formaldehyde consumed was greatly in excess of that predicted for the formation of methylol groups. A possible explanation is that in the presence of sodium hydroxide, which was necessary to dissolve the extract, that formaldehyde underwent a Cannizzaro reaction forming methanol and formic acid.

TABLE A-1

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
PLYWOOD ADHESIVE MIXES FOR CONTROLS AND 30%
SUBSTITUTION OF PHENOLIC RESIN BY EXTRACT

	Standard Plywood Adhesive Mix[a] g	Control 80g Batch Size g	30% Substitution of Extract g	30% Substitution of Extract With 10% Added Paraformaldehyde g
extract	-	-	5.5	5.5
sodium hydroxide, 14% solution	-	-	10.3 ml	10.3 ml
resin	-	-	36.8	36.8
resin[b] or resin plus extract and NaOH	1150	26.9	26.9	26.9
water	450	10.5	10.5	10.5
corn cob filler	350	6.1	6.1	6.1
-MIX 2-3 MINUTES-	mix	mix	mix	mix
wheat flour	100	4.4	4.4	4.4
soda ash	70	1.6	1.6	1.6
-MIX 15-20 MINUTES-	mix	mix	mix	mix
resin	1100	25.7	25.7	25.7
water	200	4.7	4.7	4.7
paraformaldehyde	-	-	-	0.28
water	-	-	-	2.4 ml
TOTAL WEIGHT	3420	80	80	83
TOTAL: resin or resin plus extract and NaOH	2250[c]	53	53	53

a Forintek Canada Corp., Western Laboratory
b Net P.F. (35% nominal) - 23%.
c 35% Phenol-formaldehyde.

TABLE A-2

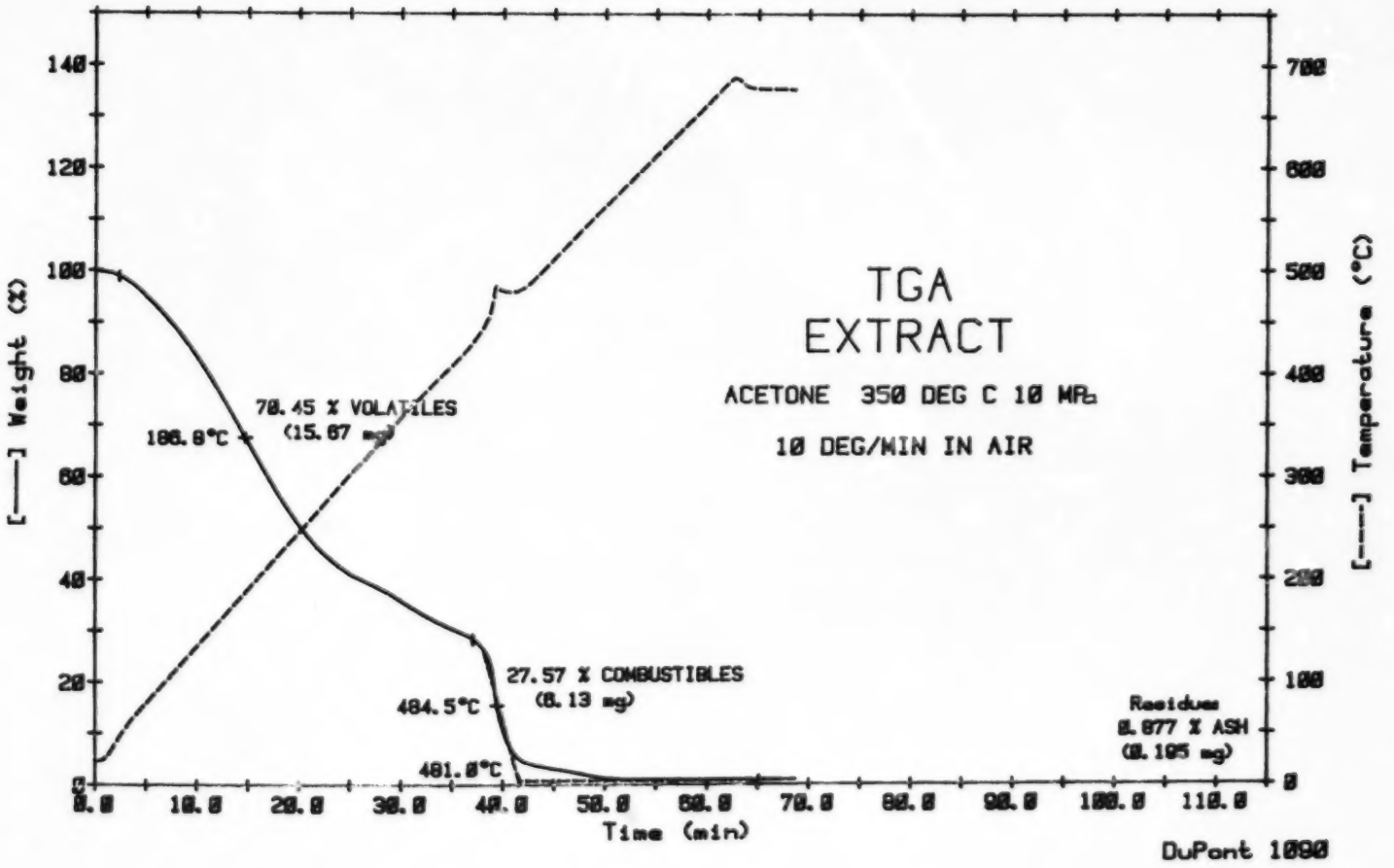
SUPERCRITICAL GAS EXTRACTION OF CEDAR:
EFFECT OF BATCH SIZE ON GLUE BOND QUALITY OF CONTROLS

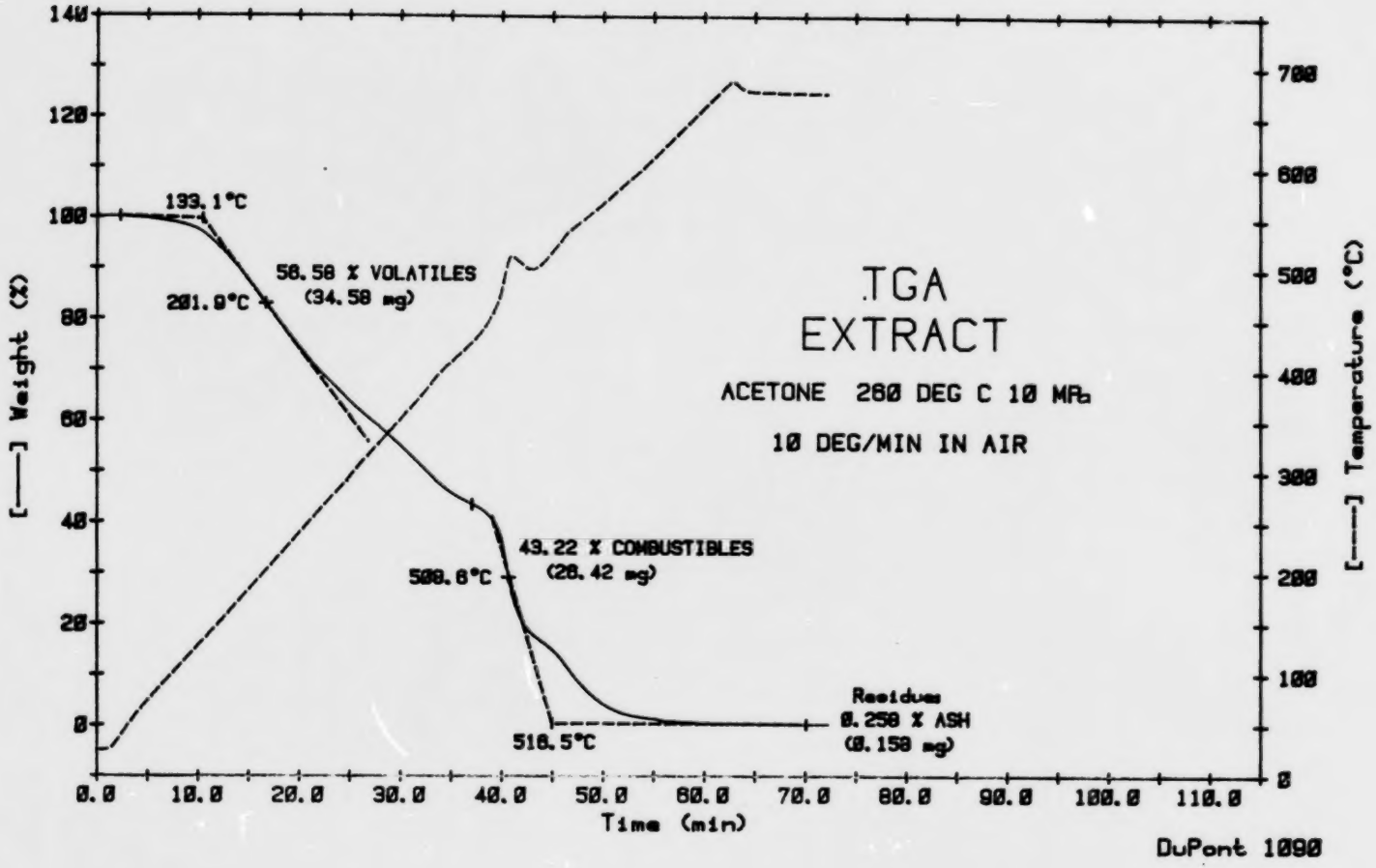
Description	Batch Size g	Viscosity cps	Dry Test		Wet Test	
			Strength MPa	Wood Failure %	Strength MPa	Wood Failure %
Standard Plywood	855	1180	2.28	98	1.38	80
Adhesive mix	855	-[a]	1.79	99	1.10	92
refer to Table A-1	80	1570	2.14	95	1.45	94
	80	1870	1.79	98	1.31	91
	80	1780	1.86	99	1.31	94

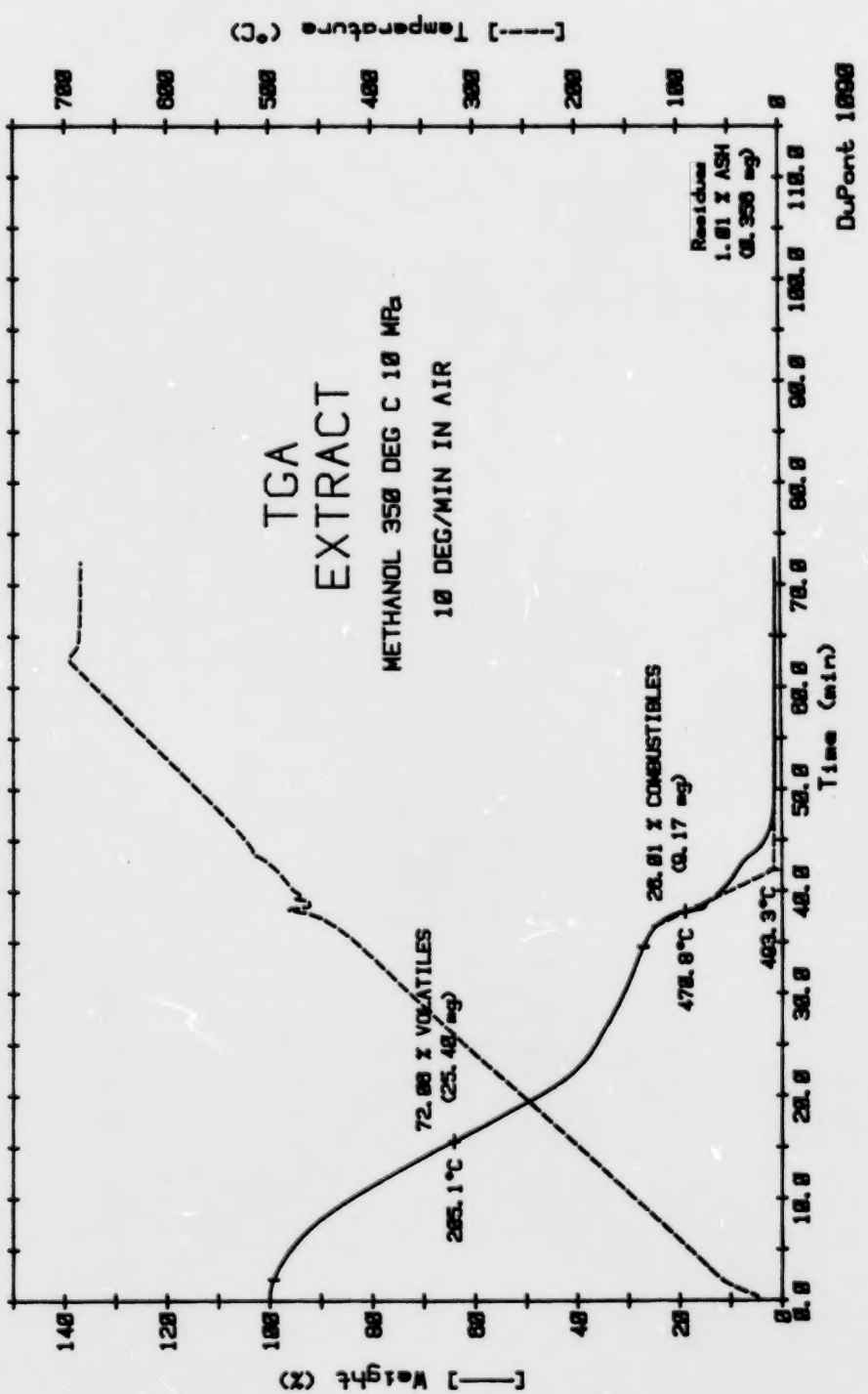
[a] not measured.

APPENDIX B

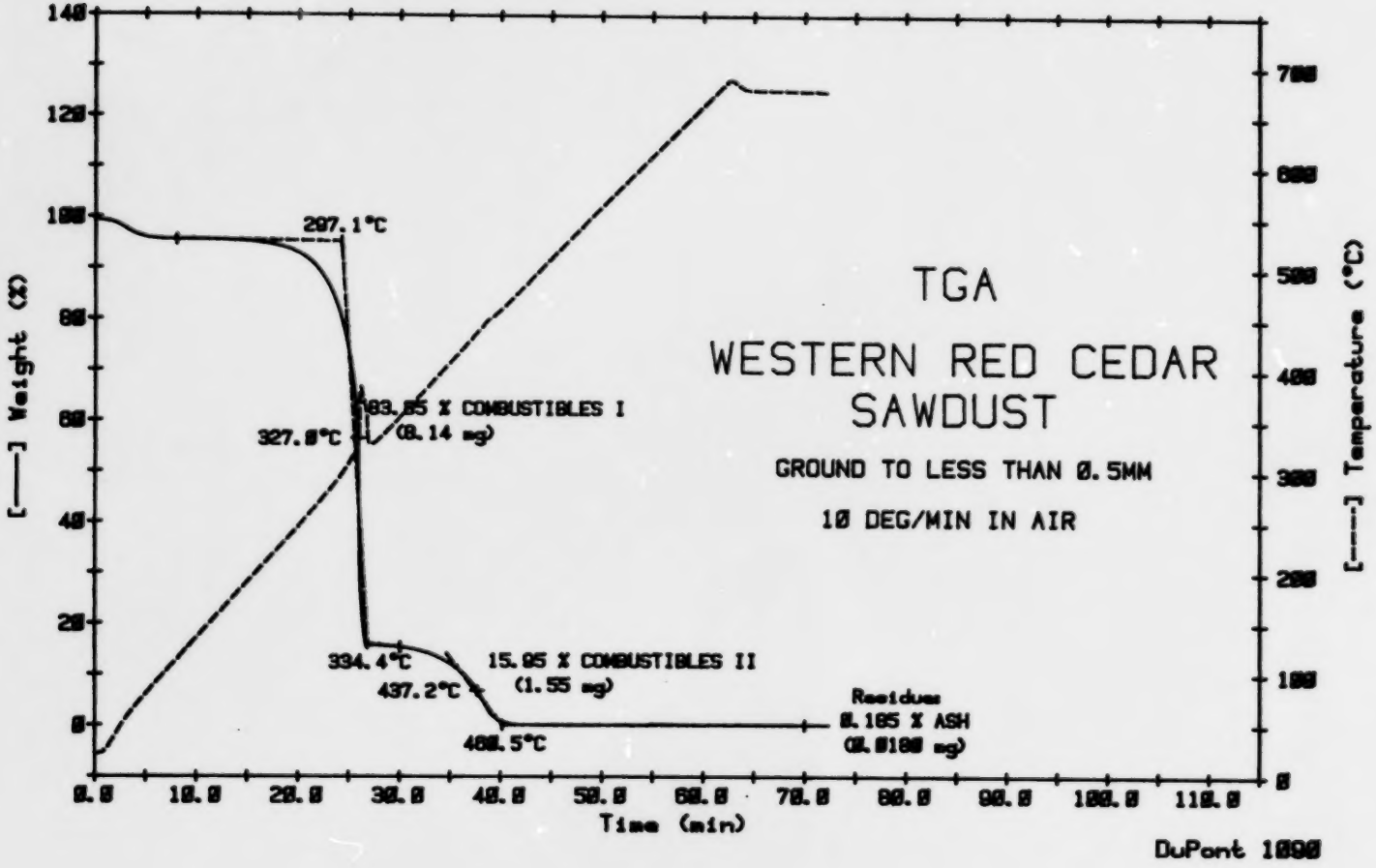
THERMOGRAVIMETRIC ANALYSIS OF SUPERCRITICAL GAS EXTRACTS, RESIDUES AND CEDAR SAWDUST


TGA
EXTRACT
ACETONE 350 DEG C 10 MPa
10 DEG/MIN IN AIR
70.45 % VOLATILES
(15.67 mg)
186.8°C
27.57 % COMBUSTIBLES
(6.13 mg)
484.5°C
481.8°C
Residue
0.977 % ASH
(0.195 mg)
[——] Weight (%)
[----] Temperature (°C)
Time (min)
DuPont 1090

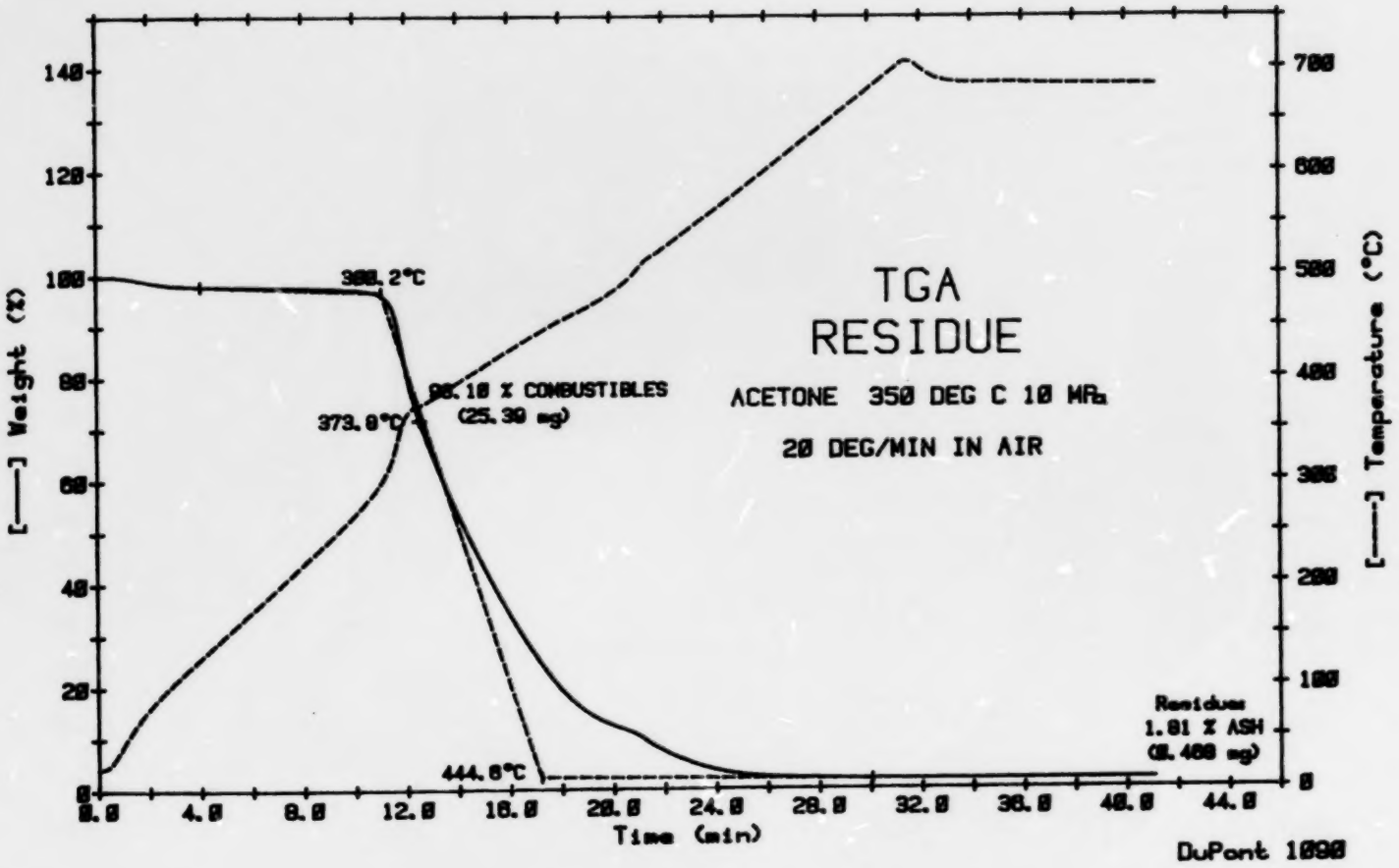

TGA
EXTRACT
ACETONE 260 DEG C 10 MPa
10 DEG/MIN IN AIR
133.1°C
58.58 % VOLATILES
(34.58 mg)
281.9°C
43.22 % COMBUSTIBLES
(26.42 mg)
508.6°C
Residue
0.258 % ASH
(0.158 mg)
516.5°C
[——] Weight (%)
[——] Temperature (°C)
Time (min)
DuPont 1090

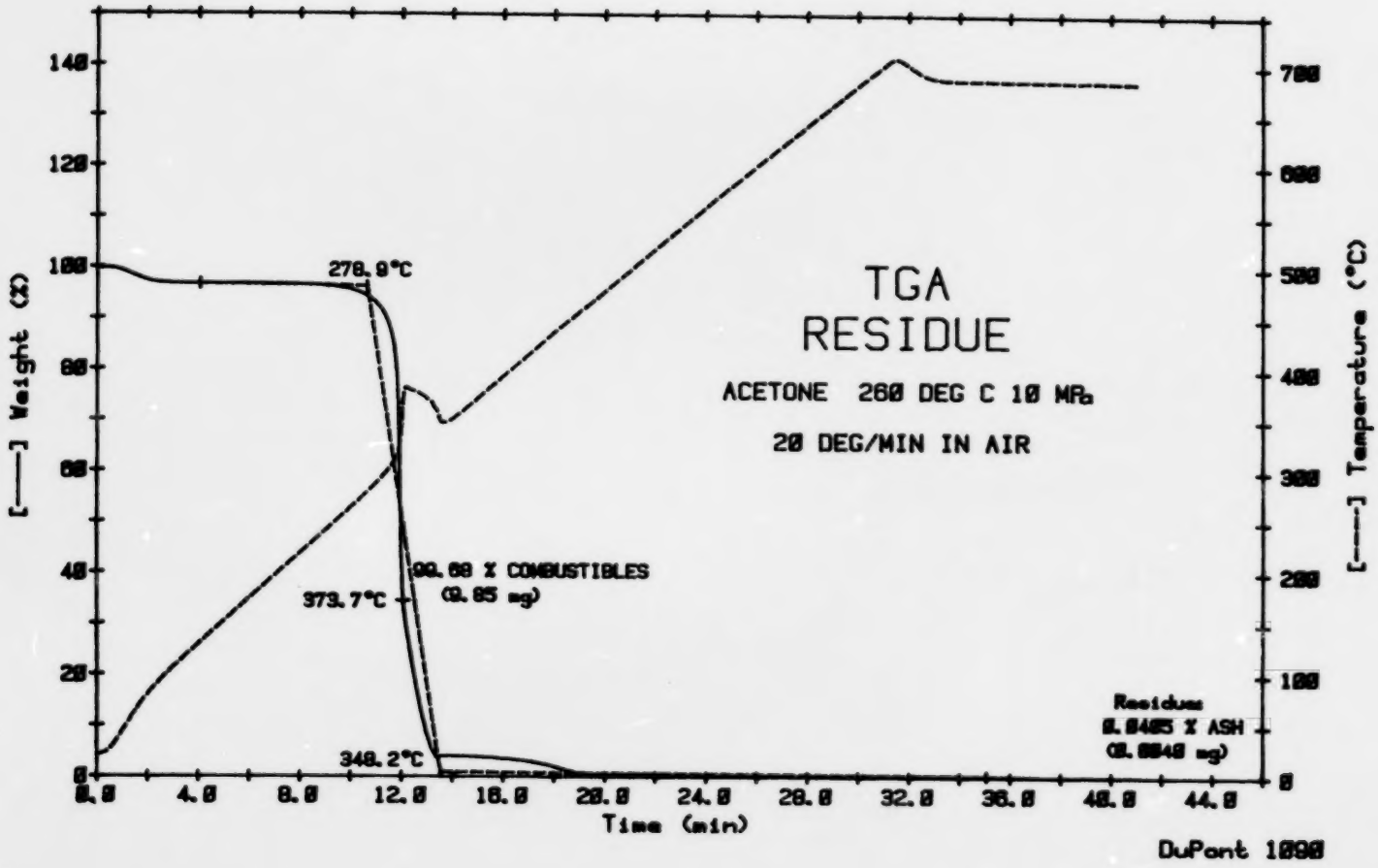

TGA
EXTRACT
METHANOL 350 DEG C 10 MPa
10 DEG/MIN IN AIR
72.88 % VOLATILES
(25.48 mg)
285.1°C
28.01 % COMBUSTIBLES
(9.17 mg)
478.8°C
463.3°C
Residue
1.81 % ASH
(0.358 mg)
Weight (%)
Temperature (°C)
Time (min)
DuPont 1090

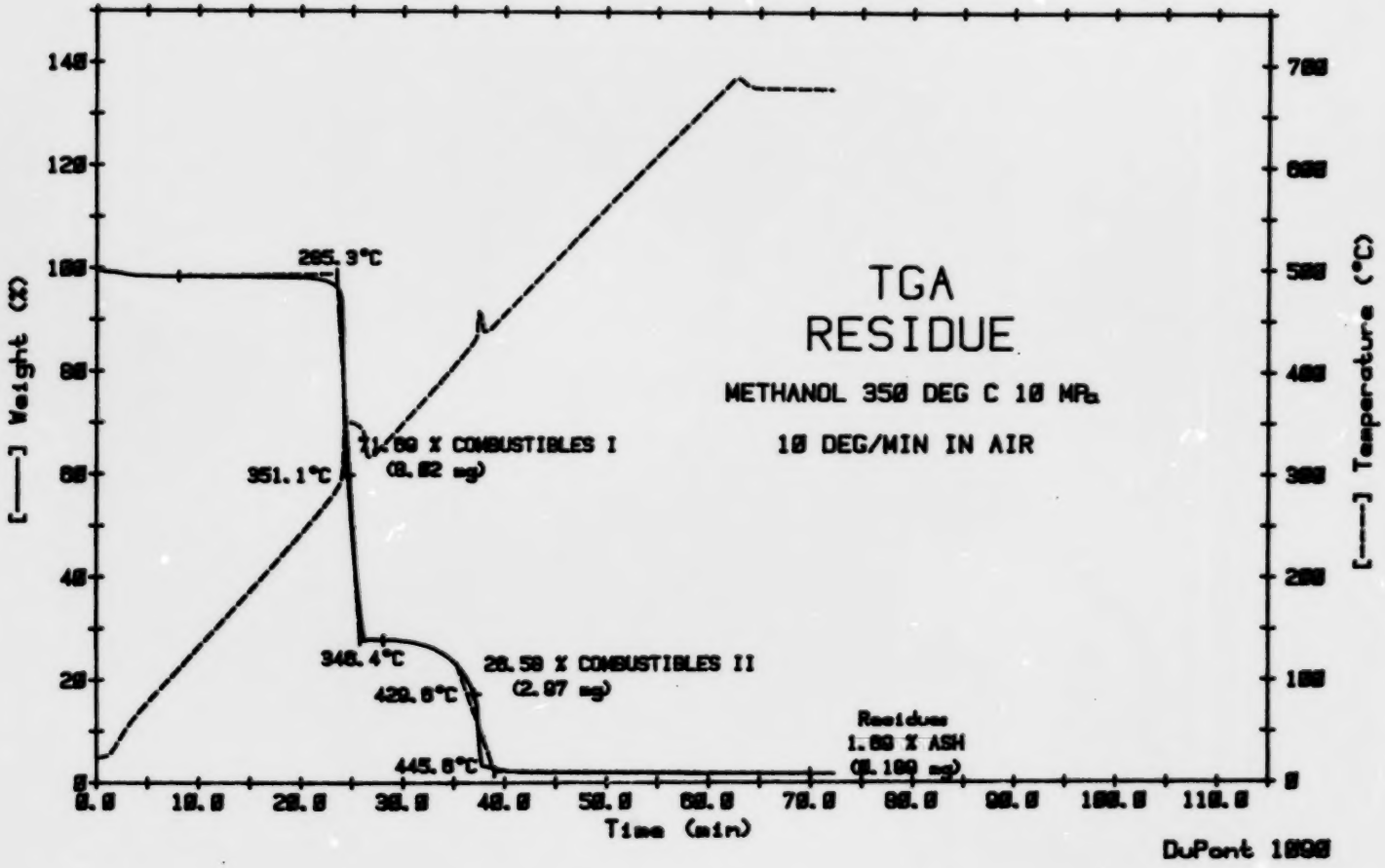
TGA


TGA
WESTERN RED CEDAR
SAWDUST
GROUND TO LESS THAN 0.5MM
10 DEG/MIN IN AIR
297.1°C
327.8°C
83.85 % COMBUSTIBLES I
(8.14 mg)
394.4°C
437.2°C
15.05 % COMBUSTIBLES II
(1.55 mg)
488.5°C
Residue
0.105 % ASH
(0.0108 mg)
[——] Weight (%)
[----] Temperature (°C)
Time (min)
DuPont 1090

TGA


TGA
RESIDUE
ACETONE 350 DEG C 10 MPa
20 DEG/MIN IN AIR
388.2°C
98.18 % COMBUSTIBLES
(25.39 mg)
373.8°C
444.6°C
Residue
1.81 % ASH
(0.468 mg)
[——] Weight (%)
[——] Temperature (°C)
Time (min)
DuPont 1090


TGA
RESIDUE
ACETONE 260 DEG C 10 MPa
20 DEG/MIN IN AIR
278.9°C
373.7°C
348.2°C
99.60 % COMBUSTIBLES
(9.85 mg)
Residue:
0.8465 % ASH
(0.0848 mg)
[——] Weight (%)
[——] Temperature (°C)
Time (min)
DuPont 1090


TGA
RESIDUE
METHANOL 350 DEG C 10 MPa
10 DEG/MIN IN AIR
285.3°C
71.69 % COMBUSTIBLES I
(8.82 mg)
351.1°C
348.4°C
28.59 % COMBUSTIBLES II
(2.97 mg)
429.8°C
445.6°C
Residue
1.89 % ASH
(0.189 mg)
[——] Weight (%)
[——] Temperature (°C)
Time (min)
DuPont 1090

APPENDIX C

DETAILED COST ESTIMATE OF AN 800 BARREL/DAY PLANT

DETAILED COST ESTIMATE OF AN 800 BARREL/DAY PLANT

- Feedstock wood or hog fuel (zero cost delivered)

- Five reactors 0.82 m (2.7') i.d. x 30 m (98') vertical, lined with 0.15 m (6") 316 ss, supported by reinforced concrete.

- One steam boiler, char and waste gas fired, (HP steam at 400°C) to evaporate 125 tonne (138 tons) per hour acetone

- One 3-stage countercurrent heat exchanger

- One condenser system comprising:

  - knockout section, 1.5 MPa (218 psig)
  - foul water condenser, 0.7 MPa (102 psig)
  - acetone condenser, atmospheric

- Associated structural steel, connections, piping, valves, electrical service and HVAC.

- Receiving, handling and five day live storage for 500 tonne (550 ton) per day feedstock (O.D. basis).

- Product storage vessels

- No allowance for greenfields' site.

INSTALLATION COSTS

1.	Steam boiler, conventional (installed cost) . . .	$ 3.2 x 10^6
2.	Heat exchanger	2.0 x 10^6
3.	Reactors (steel in place at $11/kg, Multiply by 2 for structural support and concrete reinforcement)	
	Five reactors at 0.52 x 10^6 each	2.6 x 10^6
4.	Condenser system, electrical, piping, HVAC . . . 25% of equipment cost = 0.25 x 7.8 x 10^6	2.0 x 10^6
5.	Onsite services (installation cost of . . . . . reactors, condensers and interconnects) equivalent to equipment cost, excluding boiler (sum of 2, 3 and 4).	6.6 x 10^6
6.	Acetone inventory(1) (8:1 ratio solvent . . . . . to dry feed, 4,000 tonne at $728/tonne)	2.9 x 10^6
7.	Working capital (25% of 1, 2, 3, 4, 5 & 6) . . . 0.25 x 19.3 x 10^6	4.8 x 10^6
	TOTAL INSTALLATION COST	$24.1 x 10^6

OPERATING COSTS PER BARREL OF PRODUCT(2)

1.	Twenty year write-off at 25% per year, to annual capital charge of:	
	$\frac{24.1 \times 10^6 \times 0.25}{800 \times 300_{(3)}}$	$25.1/bbl(equiv)
	Cost - Capital Depreciation	$25.1/bbl(equiv)
2.	Labour: 13 men per shift, 3 shifts per day, $20.00 per hour, 8 hours per day, $6,240/day for 800 barrels	$ 7.8/bbl(equiv)

3.	Acetone loss:	2.0% of dry feed 10 tonne per day at $728/tonne for 800 barrels	$9.9/bbl(equiv)
		OVERHEAD COST	$16.9/bbl(equiv)

PRODUCT COST

Capital Cost	$25.1/bbl(equiv)
Overhead Cost	$16.9/bbl(equiv)
PRODUCT COST	$42.0/bbl(equiv)

(1) Acetone cost $.33/lb
Chemical Marketing Report, January 4, 1982.

(2) Product yield based on calorific equivalence at 6×10^6 Btu/bbl of oil.

In Imperial Units:

$$\text{Barrels/day} = \frac{550 \text{ tpd. dry feed} \times 0.40 \text{ yield} \times 2000 \text{ lbx} \times 10800 \text{ Btu/lb}}{6 \times 10^6 \text{ Btu/bbl of oil}}$$

$$= 792 \text{ barrels/day (oil equiv.)}$$

(3) Based on 300 working days.

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
SENSITIVITY OF EXTRACT COST
TO ACETONE INVENTORY
(Solvent loss assumed to be 2% of dry feed)

	Solvent Inventory, Ratio to Dry Feed			
	3:1	5:1	8:1	10:1
Steam boiler	3.2×10^6	3.2×10^6	3.2×10^6	3.2×10^6
Heat exchanger	2.0×10^6	2.0×10^6	2.0×10^6	2.0×10^6
Reactors	2.6×10^6	2.6×10^6	2.6×10^6	2.6×10^6
Condensers,etc.	2.0×10^6	2.0×10^6	2.0×10^6	2.0×10^6
Onsite services	6.6×10^6	6.6×10^6	6.6×10^6	6.6×10^6
Acetone inventory	1.1×10^6	1.8×10^6	2.9×10^6	3.6×10^6
Working capital	4.4×10^6	4.6×10^6	4.8×10^6	5.0×10^6
TOTAL INSTALLATION COST	$\$21.9 \times 10^6$	$\$22.8 \times 10^6$	$\$24.1 \times 10^6$	$\$25.0 \times 10^6$
Labour	\$ 7.8/bbl (equiv)	7.8	7.8	7.8
Acetone loss (2% of dry feed)	\$ 9.1/bbl (equiv)	9.1	9.1	9.1
OVERHEAD COST	\$16.9/bbl (equiv)	16.9	16.9	16.9
Capital Cost	\$22.8/bbl (equiv)	23.8	25.1	26.0
Overhead Cost	\$16.9/bbl (equiv)	16.9	16.9	16.9
PRODUCT COST	\$39.7/bbl (equiv)	40.7	42.0	42.9

SUPERCRITICAL GAS EXTRACTION OF CEDAR:
SENSITIVITY OF EXTRACT COST TO ACETONE LOSS
(Solvent inventory assumed to be 8:1 ratio of acetone to dry feed)

	Solvent Loss, Percent of Dry Feed				
	1%	2%	3%	4%	5%
Steam boiler	3.2×10^6	3.2×10^6	3.2×10^6	3.2×10^6	3.2×10^6
Heat exchanger	2.0×10^6	2.0×10^6	2.0×10^6	2.0×10^6	2.0×10^6
Reactors	2.6×10^6	2.6×10^6	2.6×10^6	2.6×10^6	2.6×10^6
Condensers,etc.	2.0×10^6	2.0×10^6	2.0×10^6	2.0×10^6	2.0×10^6
Onsite services	6.6×10^6	6.6×10^6	6.6×10^6	6.6×10^6	6.6×10^6
Acetone inventory (8:1 to dry feed)	2.9×10^6	2.9×10^6	2.9×10^6	2.9×10^6	2.9×10^6
Working Capital	4.8×10^6	4.8×10^6	4.8×10^6	4.8×10^6	4.8×10^6
TOTAL INSTALLATION COST	$\$24.1 \times 10^6$	24.1×10^6	24.1×10^6	24.1×10^6	24.1×10^6
Labour	\$ 7.8/bbl (equiv)	7.8	7.8	7.8	7.8
Acetone loss	\$ 4.6/bbl (equiv)	9.1	13.7	18.2	22.8
OVERHEAD COST	\$12.4/bbl (equiv)	16.9	21.5	26.0	30.6
Capital cost	\$25.1/bbl (equiv)	25.1	25.1	25.1	25.1
Overhead cost	\$12.4/bbl (equiv)	16.9	21.5	26.0	30.6
PRODUCT COST	\$37.5/bbl (equiv)	42.0	46.6	51.1	55.7

APPENDIX D

SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:

ELEMENTAL ANALYSIS OF WAXES OBTAINED BY SUPERCRITICAL GAS AND SOLVENT EXTRACTIONS

SUPERCRITICAL GAS EXTRACTION OF DOUGLAS-FIR BARK:
ELEMENTAL ANALYSIS OF WAXES

Description	Pressure MPa	Elemental Analysis			
		%C	%H	%N	%O[a]
Silvacon 387, MBB					
Nitrous oxide	21	74.86	11.42	0.04	13.68
" " "	62	74.71	11.21	0.04	14.04
Carbon dioxide	21	77.37	11.64	0.04	10.95
" " "	62	76.55	10.98	0.04	12.43
Petroleum ether					
6 hours		77.14	11.42	0.05	11.39
40 hours		76.09	11.20	0.04	12.67
Ethyl acetate		66.74	8.47	0.03	24.76
Silvacon 383					
Nitrous oxide	21	74.27	12.07	0.12	13.54
" " "	62	74.27	11.55	0.13	14.05
Carbon dioxide	21	77.36	11.94	0.03	10.67
" " "	62	76.35	11.19	0.04	12.42
Petroleum ether					
6 hours		75.02	11.12	0.05	13.81
40 hours		73.87	11.08	0.03	15.02

[a] Calculated by difference.

ABSTRACT OF THE ABSTRACT
CHEMICALS FROM FOREST PRODUCTS BY SUPERCRITICAL GAS EXTRACTION

Supercritical acetone and methanol gave high yields of tarry products from wood. Supercritical gases, including carbon dioxide, extracted naval stores and waxes.

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